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TABLE OF CONTENTS

MINERAL SCIENCE SECTION

Method/Technique	Page Header	Section
The Technique of Sample Preparation	*Sample Preparation*	MS1-1
Assay Sample Preparation	*Assay Preparation*	MS1-2
Whole-rock Sample Preparation	*Whole-rock Preparation*	MS1-4
Carbonate and Trace Element Preparation for Soils	*Carbonate Preparation*	MS2-1
Conodont Separation and Preparation	*Conodont Preparation*	MS3-1
Grain-Size Analysis		
Introduction	*Grain-size Analysis*	MS4-1
Conventional ASTM D422-72 Grain-Size Analysis	*Grain-size Analysis-1*	MS4-2
Grain-Size Analysis by Particle Sizing	*Grain-size Analysis-2*	MS4-10
Atterberg Limits (ASTM D423-66)	*Atterberg*	MS5-1
Separation of Minerals Using Heavy Liquids	*Heavy Liquid Separation*	MS6-1
Mineral Separation Using the Frantz Magnetic Separator	*Magnetic Separation*	MS7-1
Rock and Mineral Identification for Prospectors and Geologists	*Mineral Identification*	MS8-1
Optical Mineralogy	*Optical Mineralogy*	MS9-1
X-ray Powder Diffraction	*XRD*	M10-1
X-ray Diffraction Identification	*Clay XRD*	MS11-1
Determination of Specific Gravity	*Specific Gravity*	MS12-1
Determination of Moisture Content of Soils (ASTM D2216-71)	*Soil Moisture*	MS13-1
Fire Assay		
Introduction	*Fire Assay*	MS14-1
Conventional Fire Assay Method for Au and Ag	*Fire Assay-1*	MS14-2
Fire Assay Preconcentration for Determination of Au, Pt, Pd by GFAAS	*Fire Assay-2*	MS14-3
Nickel Sulphide Fire Assay	*Fire Assay-3*	MS14-4
Normative Programs	*Norms*	MS15-1
Alknorm for Feldspathoidal and Melilitic Igneous Rocks	*Alknorm*	MS16-1

ELEMENTAL ANALYSIS SECTION

Method/Technique	Page Header	Section
Protocols for Sample Digestion and Analytical Determination	*Protocols*	EA1-1
Sample Dissolution	*Sample Dissolution*	EA2-1
Graphite Furnace Operating System	*Graphite Furnace*	EA3-1
Operation of the Atomic Absorption Spectrometer	*Varian AA775*	EA4-1
Liquid Handling System	*Liquid Handling System*	EA5-1
Determination of Major Elements by XRF		
The Philips PW14OO Fluorescence Spectrometer System	*Major - XRF*	EA6-1
Determination of the Major Elements (M1, M2, M3) X-ray Fluorescence Spectroscopy	*Majors - XRF*	EA6-6
Appendix A: LOI Corrections	*Majors - XRF*	EA6-14
Appendix B: Method Development	*Majors - XRF*	EA6-16
Appendix C: Setting Up an Analytical Package	*Majors - XRF*	EA6-21
Determination of Major Elements (SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO) Flame Atomic Absorption Spectroscopy	*Majors - AA*	EA7-1
Determination of Major Elements (SiO_2, Al_2O_3, CaO, MgO) Classical (Gravimetric) Method	*Majors - Classical*	EA8-1
Determination of Titanium as (TiO_2) Colorimetric Method	*Titanium*	EA9-1
Determination of Phosphorus (P_2O_5) Colorimetric Method	*Phosphorus*	EA10-1
Determination of Sodium and Potassium Flame Photometric Method	*Sodium/Potassium*	EA11-1
Determination of ±Water Combustion/Infrared Absorption Method	*Water*	EA12-1
Determination of Carbon and Sulphur Combustion/Infrared Absorption Method	*Carbon/Sulphur*	EA13-1
Determination of Total Fe Volumetric (Titrimetric) Method	*Total Fe*	EA14-1
Determination of Ferrous Iron Titrimetric Method	*Ferrous*	EA15-1

Method/Technique	Page Header	Section
Determination of Trace Elements (T3) X-ray Fluorescence Spectroscopy	*Traces - XRF*	EA16-1
Appendix A: Trace Element Determinations - Measurement Programs	*Traces -XRF*	EA16-4
Measurement Program for Gallium	*Traces -XRF*	EA16-7
Measurement Program for Tantalum	*Traces - XRF*	EA16-9
Measurement Program for Ce, La, and Nd	*Traces - XRF*	EA16-11
Measurement Program for Cesium	*Traces - XRF*	EA16-13
Appendix B: Mass Absorption Calculation Program for Apple IIe	*Traces - XRF*	EA16-14
Appendix C: Mass Absorption Values for Selected Silicates SRM's	*Traces - XRF*	EA16-18
Appendix D: MA Factors (Sr Kα Wavelength)	*Traces - XRF*	EA16-19
Appendix E: XRF Detection Limit Calculation	*Traces - XRF*	EA16-20
Appendix F: Rate Correction Parameters	*Traces - XRF*	EA16-21
Determination of Trace Elements (Co, Cu, Cr, Ni, Pb,Zn, Ba, Li, Ag, Cd, Mn, Fe) Atomic Absorption Spectroscometry	*Traces - AA*	EA17-1
Determination of Trace Elements by ICP-OES		
Overview of Trace Element Determination by ICP Optical Emission Spectroscopy	*Traces - ICP-OES*	EA18-1
The Trace 2 (T2) Package	*Traces - ICP-OES*	EA18-14
Appendix A: Generation of T2 Final Reports	*Traces - ICP-OES*	EA18-21
Aqueous Samples Analysis Package	*Traces - ICP-OES*	EA18-24
Tentative Spectroscopic Analysis Package (TSPA)	*Traces - ICP-OES*	EA18-25
Appendix A: Generation of the TSPA Certificates	*Traces - ICP-OES*	EA18-26
Determinatio of Trace Elements by ICP-MS		
Sample Preparation for the T4 and T5 ICP-MS Package	*Traces ICP-MS*	EA19-1
The Elan-250	*Traces - ICP-MS*	EA19-5
Trace 4 (T4) Elements	*Traces - ICP-MS*	EA19-13
Trace 5 (T5) Elements	*Traces - ICP-MS*	EA19-18
Determination of the Rare Earth Elements (La, Ce, Nd, Sm, Eu, Yb, Lu) Thorium, Tantalum, Hafnium, Uranium, and Scandium Instrumental Neutron Activation Analysis	*Traces - NAA*	EA20-1
Determination of Gold, Platinum and Palladium Graphite Furnace Atomic Absorption Spectroscopy	*Au, Pt, Pd*	EA21-1
Determination of Gold in Natural Waters Solvent Extraction and Electrochemical Atomization Method	*Gold*	EA22-1
Determination of Fluoride Automated Colorimetric Method	*Flouride*	EA23-1

Method/Technique	Page Header	Section
Determination of Chloride Automated Colorimetric/Flow Injection Analysis Method	*Chloride*	EA24-1
Determination of Arsenic, Antimony and Bismuth Hybrid Generation - Atomic Absorption Spectrometry	*As, Sb, Bi*	EA25-1
Determination of Selenium Hybrid AAS - Automated Flow Injection Analysis Method	*Selenium*	EA26-1
Determination of Mercury Cold Vapor Flameless Atomic Absorption Method	*Mercury*	EA27-1
Determination of Carbonate-Carbon (CO_2) Coulometric Method	*Carbonate Carbon*	EA28-1
Determination of Moisture	*Moisture*	EA29-1
Determination of Acid Insoluable Residue	*Acid*	EA30-1
Determination of the Calcite to Dolomite Ratio Chittick Apparatus Method	*Chittick*	EA31-1

THE TECHNIQUE OF SAMPLE PREPARATION

The preparation of samples represents the single most important step in the analysis of geological materials. Undetected errors in the handling of rocks such as: sample mixup, contamination with dust or rock fragments, and introduction of components from the grinding equipment can lead to erroneous conclusions in the interpretation of the data.

The Laboratories uses two sample preparation procedures on a routine basis:

1. Preparation of samples for assay work, and

2. Preparation of samples for whole-rock geochemical analysis.

ASSAY SAMPLE PREPARATION

Introduction:

Assay preparation is employed whenever a geologist or prospector requires an indication of base or precious metal potential. Assay samples are given high priority and a rapid turnaround. The assay preparation should not be used when geologists require detailed geochemical work.

Safety advisory:

When working in the grinding area:

1. Wear a full face-piece respirator unit to eliminate the possibility of silicosis; THIS LABORATORY AREA IS MONITORED UNDER A SILICA CONTROL PROGRAM.
2. Wear a face shield or safety goggles.
3. Wear ear muffs. Sound levels from the jaw crushers can exceed 100 dB.
4. Wear a laboratory coat at all times in the area, and take it off before leaving.
5. Do not eat, smoke, or drink in the grinding area.
6. Be aware of samples requiring special handling. These samples will be flagged, e.g. As/Pb containing. If you identify a potential hazard then it is your responsibility to flag the samples.
7. Ensure that the main exhaust system is switched on during grinding operations.
8. Observe safety procedures specific to each piece of equipment. Ensure that the lids on the jaw crushers are closed immediately after the sample is introduced. The mills on the vibratory ring-pulverizer (also called a Swing-Miller) should be firmly secured before the equipment is switched on.
9. Uncontrolled cleaning of equipment and clothes using compressed air is not acceptable.

Technique:

Assay sample preparation involves the following procedures:

1. Sorting of samples in preparation for grinding
2. Crushing the samples sequentially using a jaw crusher
3. Riffling to split the samples - retaining one split for grinding and another split as a back-up
4. Grinding the split in the mill on the vibratory ring-pulverizer for the appropriate length of time.
5. Removing pulp, after grinding, onto glazed paper and transferring to pulp bags.

General comments

Ensure that the mill is cleaned before and after use with compressed air in the blow-out area. When compressed air will not remove the dust, use quartzite as a cleaner. The grinding area should be kept clean by using the central vacuum unit.

Apparatus:

- Containers for laying out the samples on the bench-top in a systematic fashion
- Large jaw-crusher with steel plates
- Riffle to split samples
- Vibratory ring-pulverizers equipped with two chrome-steel mills (a tungsten carbide and ceramic mill can be used if specifically requested). When large quantities of pulp are required, two large chrome-steel mills are available.

Reagents:

- Quartzite

Procedures:

1. Samples are collected from the sample reception area along with a series of labels and a list of samples. Any special instructions accompanying samples should be clarified with the sample reception technician.
2. Labels are affixed to bags and/or containers used to store crushed rock and final pulp.
3. Samples and bags are placed in previously cleaned containers in ascending order of sample number. Any materials affixed to the samples, except markings, are removed.

4. Wet samples are dried in a hot-air drier.
5. The exhaust fan is switched on, and the gate to the jaw crusher is opened. The jaw crusher is cleaned using compressed air and a wire brush.
6. Observing necessary safety precautions, the rock sample is crushed.
7. The crushed sample is split in the vented riffler.
8. Reject material is retained in a pulp bag.
9. About 100 g of crushed rock is placed in a cleaned chrome-steel mill. The mill is secured to the vibratory ring-pulverizer, and ground for an appropriate length of time (depending on hardness). Typically, 90 seconds is sufficient.
10. The mill is transferred to the blow-out area, and the rock powder is collected on glazed paper, and transfered to a previously labelled pulp bag.

General comment. Use two chrome-steel mills so that one is grinding while the other is being cleaned with compressed air.

Quality Control:

When the mill cannot be cleaned with compressed air, quartzite is used.

Assay grinding is used in the preparation of samples for geologists and prospectors who do not require whole-rock geochemical analysis.

A record is kept of the sequence in which the samples are ground, and of the identity number of the container used for each sample. This record is of use if a high grade sample is identified in the analytical stage; it allows contamination of subsequent samples to be checked.

Productivity:

Typically, a technician can complete forty-five assay grinds per day. One hundred assay grinds are possible under ideal sample conditions.

WHOLE-ROCK SAMPLE PREPARATION

Introduction:

This preparation technique is applied whenever the geologist requires detailed whole-rock geochemical analysis. Samples submitted in batches for whole-rock analysis are usually given a job number.

Safety advisory:

Refer to the safety advisory as detailed in the Assay Preparation method (Page M1-1).

Technique:

Whole-rock sample preparation involves the following procedures:

1. Sorting of samples in preparation for grinding
2. Determining specific gravity for each sample
3. Crushing the samples sequentially using a jaw crusher (retaining a hand sample)
4. Riffling to split sample - retaining one split for grinding and another split as a back-up
5. Grinding the split in a mill on a planetary ball mill for an appropriate length of time
6. Sieving the pulp and re-grinding the material (>-170 mesh)
7. Removing pulp, after grinding, onto glazed paper and transferring to labelled bottle

General comment. Ensure that equipment is cleaned before and after use with quartzite as a cleaner, and compressed air in the blow-out area. The grinding area should be kept clean by using the central vacuum unit.

Apparatus:

- Containers for laying out the samples on the bench-top in a systematic fashion
- Balances for the determination of specific gravity
- Small jaw-crusher with steel plates
- Riffle to split samples
- Planetary ball mill (99.8% pure alumina)
- 170 mesh nylon sieve
- Central vacuum unit

The Braun pulverizer equipped with ceramic plates is sometimes used for coarse-grained jaw crushed rock to improve mineral liberation for mineral separation procedures.

Reagents:

- Acetone
- Quartzite

Procedures:

1. Samples are collected from the sample reception area along with a series of labels and a copy of the job sheet. Any special instructions accompanying samples should be clarified with the sample reception technician.
2. Labels are affixed to containers used to store crushed rock and final pulp. The sample preparation technician assigns a laboratory number in addition to the sample number, which determines the sequence in which the samples are ground.
3. Hand samples of the rocks are retained in the original sample bags.
4. The remainder of the samples are placed in previously cleaned containers in ascending order of sample number. Any materials affixed to the samples including tape, enamel, lichen and paint are removed. **NOTE:** If the samples are weathered or altered, the technician should inform the sample reception technician, who will contact the geologist to ascertain whether the weathered material should be removed. **It is up to the geologist to remove weathered surfaces and other markings.**
5. Wet samples are dried in a hot-air drier.
6. Specific gravity is determined (refer to the method of Determining Specific Gravity on page M12-1).
7. The exhaust fan is switched on, and the gate to the jaw crusher is opened. The jaw crusher is cleaned using compressed air and a wire brush.
8. Observing necessary safety precautions, the rock sample is crushed.
9. Crushed sample is split in the vented riffler.

10. Reject material is retained in a labelled pulp bag.

11. 100 g of crushed rock are placed in a cleaned ceramic mill along with an appropriate number of grinding balls (normally about five 20 mm, or two 30 mm and three 20 mm balls). Two or four mills are bolted onto the turntable of the planetary ball mill, the lid is closed, and the machine is switched on for a period of upto 15 minutes (depending on sample hardness).

12. The powder and ceramic balls are removed from the mill and screened through a 170 mesh nylon sieve onto a piece of glazed paper. Any material which is +170 is re-ground, until the entire sample passes a 170 mesh. The agate mortar and pestle are used when the sample is too small for re-grinding (i.e., <2g).

13. The rock powder is rolled on the glazed paper and transferred to a labelled bottle.

Quality Control:

The mills are cleaned with quartzite and compressed air.

Under an in-house quality control program, three samples in selected jobs are ground in duplicate.

A record is kept of the sequence in which the samples are ground, and of the identity number of the container used for each sample. If a high grade sample is identified during analysis, subsequent samples prepared in the same apparatus are be checked for contamination.

Productivity:

A technician should be able to complete thirty grinds (samples) per day.

CARBONATE AND TRACE ELEMENT PREPARATION FOR SOILS

Introduction:

This sample preparation procedure is used to prepare soil and regolith samples for Chittick analysis, major analysis and/or trace element analysis as described in The Elemental Analysis Section of this manual.

Procedure:

1.1. The dry sample is hand broken to pass No. 10 mesh sieve. Special care is taken not to crush any larger particles in the soil sample. The amount of sample dried depends upon the grain-size.

1.2. Soil passing the No. 10 sieve is thoroughly mixed until homogeneous. Portions of this mixture are sieved through No. 80 and No. 200 sieves. Material passing No. 200 is kept for carbonate analysis (12-15 g).

1.3. Another portion is sieved through number 120 and 400 sieves. Material passing No. 400 is kept for trace element analysis (12-15 g).

Sieves No. 80 and 120 are used to protect the fine mesh of the No. 200 and 400 sieves.

CONODONT SEPARATION AND PREPARATION

Introduction:

Conodonts are microfossils. They are used to establish the age of the strata in which they are found, and to correlate rocks in different areas.

Procedure:

1.1. Crumble the sample gently between two layers of clean paper.

1.2. Transfer the sample to a 3 or 4 liter beaker and cover with water for 2-3 days. Decant.

1.3. Add commercial H_2O_2 to just cover the sample.

1.4. Add hot water to half-fill the beaker if the sample is still coherent, otherwise proceed to step 1.5.

1.5. Add 6 g of "Calgon" and 6 g of bicarbonate of soda to the beaker containing the sample and water. This causes an exothermic reaction in which clay is dissolved and dispersed. Cold water may be added to lessen the reaction. After 30 minutes, dispersal is complete and the residue may be washed and sieved. If pyrite is present, the production of sulphuric acid is avoided by adding 6 g of sodium bicarbonate and then boiling on a hotplate until disintegration occurs.

1.6. Wash the residue through 3 sieves. An 18 mesh sieve is used to collect larger microfossils; a 85 and 170 mesh sieve is used to collect smaller microfossils.

1.7. If any undisintegrated rock fragments remain on the 18 mesh sieve, repeat steps 1.5-1.6.

1.8. Wash the residue from each sieve into filter papers in funnels, and dry the residue.

1.9. Transfer the residue to dry bottles for subsequent study.

GRAIN-SIZE ANALYSIS

Introduction:

Detailed knowledge of the physical characteristics and structural properties of soils is essential in helping engineers determine soil behavior and performance in a variety of construction conditions. Grain-size analysis is widely used in the engineering classification of soils. It is useful in assessing soil permeability and capillarity which are important considerations in predicting soil behavior in cold climates.

An important use, particularily with coarse soils, is in designing inverted fillers for dams and levees. Grain-size analysis is also used in the study of sedimentary rocks as grain-size distributions are a function of the processes forming the sediment.

Grain-size analysis may be performed by either:

1. A conventional sieve-hydrometry (ASTM D422-72) technique.

2. The use of a limited number of sieves, a particle sizing system, and a clay fraction determination by hydrometry.

The latter procedure is not well suited to samples with high clay content (greater than 25% less than 2mu in size).

Table GSA1 shows the relationship between sieve number and particle size.

TABLE GSA1. PARTICLE SIZE TABLE AND SIEVE INFORMATION

U.S. Mesh	Inches	Microns	Millimeters
4	0.187	4760	4.76
5	0.157	4000	4.00
6	0.132	3360	3.36
7	0.111	2830	2.83
8	0.0937	2380	2.38
10	0.0787	2000	2.00
12	0.0661	1680	1.68
14	0.0555	1410	1.41
16	0.0469	1190	1.19
18	0.0394	1000	1.00
20	0.0331	840	0.84
25	0.0280	710	0.71
30	0.0232	590	0.59
35	0.0197	500	0.50
40	0.0165	420	0.42
45	0.0138	350	0.35
80	0.0070	177	0.177
100	0.0059	149	0.149
120	0.0049	125	0.125
140	0.0041	105	0.105
170	0.0035	88	0.088
200	0.0029	74	0.074
230	0.0024	62	0.062
270	0.0021	53	0.053
325	0.0017	44	0.044
400	0.0015	37	0.037
500	0.0014	31	0.031

Safety advisory:

1. When sieving samples wear ear muffs, a mask and eye protection.

2. The Hiac Royco system works on the basis of laser sizing. When removing the laser sizer for cleaning, ensure the power is turned off to avoid accidental exposure to laser radiation.

METHOD 1
CONVENTIONAL ASTM D422-72 GRAIN-SIZE ANALYSIS

Method:

A conventional grain-size analysis involves the following techniques:

1. Sample preparation - drying sample and dispersing clumps
2. Separating the various size fractions - sieving and hydrometry
3. Calculating results based on measured weights

Apparatus:

- Sieves (2000, 850, 425, 250, 125 and 63 microns)
- Soil breaker
- Sedimentation cylinders (46 cm high, 6.4 cm wide)
- Thermometers (accurate to ±0.5°C)
- Hydrometer (ASTM standard hydrometer, graduated to read in either specific gravity of the suspension or grams per liter of suspension)
- Jet mixer (with electric motor producing 10,000 RPM)

Reagents:

- Sodium hexametaphosphate (deflocculating agent used to break the charge attraction of clay particles). A solution of this chemical is made by dissolving 40 g of sodium hexametaphosphate in 1 liter of distilled water

Procedure:

1. Sample preparation

1.1. The soil sample is collected from the sample reception technician along with a job sheet. The sample bag (normally of paper construction) is opened and placed into the drying cupboards for a period of at least one week.

1.2. Dry samples are removed from the driers and systematically broken using a mechanical soil breaker, and a mortar with a rubber pestle to avoid breaking individual particles.

1.3. The sample is then passed through a number 10 (2000 micron) sieve, and a sub-sample weighing 50 g (for sandy material), or 100 g (for silty or clay soils) is retained in a 250 ml capped flint glass jar. The remaining -10 mesh material is retained, and may be required for other tests.

1.4. 125 ml of the deflocculant solution (see Reagents section for preparation) is added to the sample, and is allowed to soak into the sample overnight. The sample is then transferred to a mixing container, and mixed with the jet mixer for 1 minute.

1.5. The sample is washed into a graduated cylinder which is then filled up to the level line with distilled water. Before taking any readings, each cylinder is covered with a rubber stopper and systematically inverted for a period of 1 minute to completely mix the soil suspension with the water.

1.6. At the end of 1 minute, the cylinders are set down, and hydrometry readings are taken at the following time intervals (measured from the beginning of sedimentation): 2, 5, 15, 30, 60 and 240 (4 hrs), and 1440 (24 hrs) minutes. The hydrometer scale would normally be read at the base of the meniscus, but the soil suspension makes this impossible, so the reading is taken at the top of the meniscus.

1.7. The temperature of the suspension is checked with a thermometer.

1.8. After the final reading has been taken, the sample is transferred to a No. 230 (62 micron) sieve and washed with tap water until the wash water is clear. Material left on the sieve is then dried in an oven at 110°C. This portion is then sieved. For clay samples, the following sieves are used: No. 10, 20, 40, 120, and 230. For sands, the following sieves are used: No. 10, 14, 18, 25, 35, 45, 60, 80, 120, 170 and 230.

1.9. The portion retained on each of the sieves is weighed using a balance, and the percentage passing each sieve is recorded.

1.10. Calculations are made using the results from the above procedure.

2. Calculation of results

For an ASTM hydrometer (152H), the calculation reads in grams of soil per liter of suspension.

2.1. Percentage retained on any sieve =

$$\frac{\text{Weight of soil retained}}{\text{Total weight of soil}} \times 100\%$$

2.2. Percentage finer than any sieve size =

100% – *Cumulative percentage retained*

2.3. Percentage of soil remaining in suspension at the level at which the hydrometer measures the density of the suspension =

$$\frac{R \times A}{W} \times 100\%$$

where, R = corrected hydrometer reading
A = correction factor applied to the reading of hydrometer 152H (Refer to Table GSA4)
W = Oven-dry weight of soil dispersed and used for hydrometry readings (g)

2.4. Diameter of soil particles (mm) =

$$K\sqrt{\frac{L}{T}}$$

where, K = A constant depending on the temperature of the suspension and the specific gravity of the soil particles (Refer to Table GSA2)
L = Distance from the surface of the suspension to the level at which the density of the suspension is measured (cm) (Refer to Table GSA3)
T = Interval of time from beginning of sedimentation to the taking of the reading (min.)

The results are presented graphically by plotting the diameters of the particles on a horizontal logarithmic scale and the cumulative percentage smaller than a given size on the vertical axis (Figure GSA1).

The final report should include:

1. The maximum particle size
2. The percentage passing each sieve
3. A description of the sand and gravel shape and hardness
4. Specific gravity
5. Any problems in dispersing the 1000 micron fraction

Quality control:

Analysis of the in-house Geoscience Laboratories soil standard should accompany each job. Hydrometry should be performed on a 50 g sample of the standard which can be reused.

The gradation curve for this material is shown in Figure GSA1 based on data presented in Table GSA5; and should be reproduced with a precision of 5% or better.

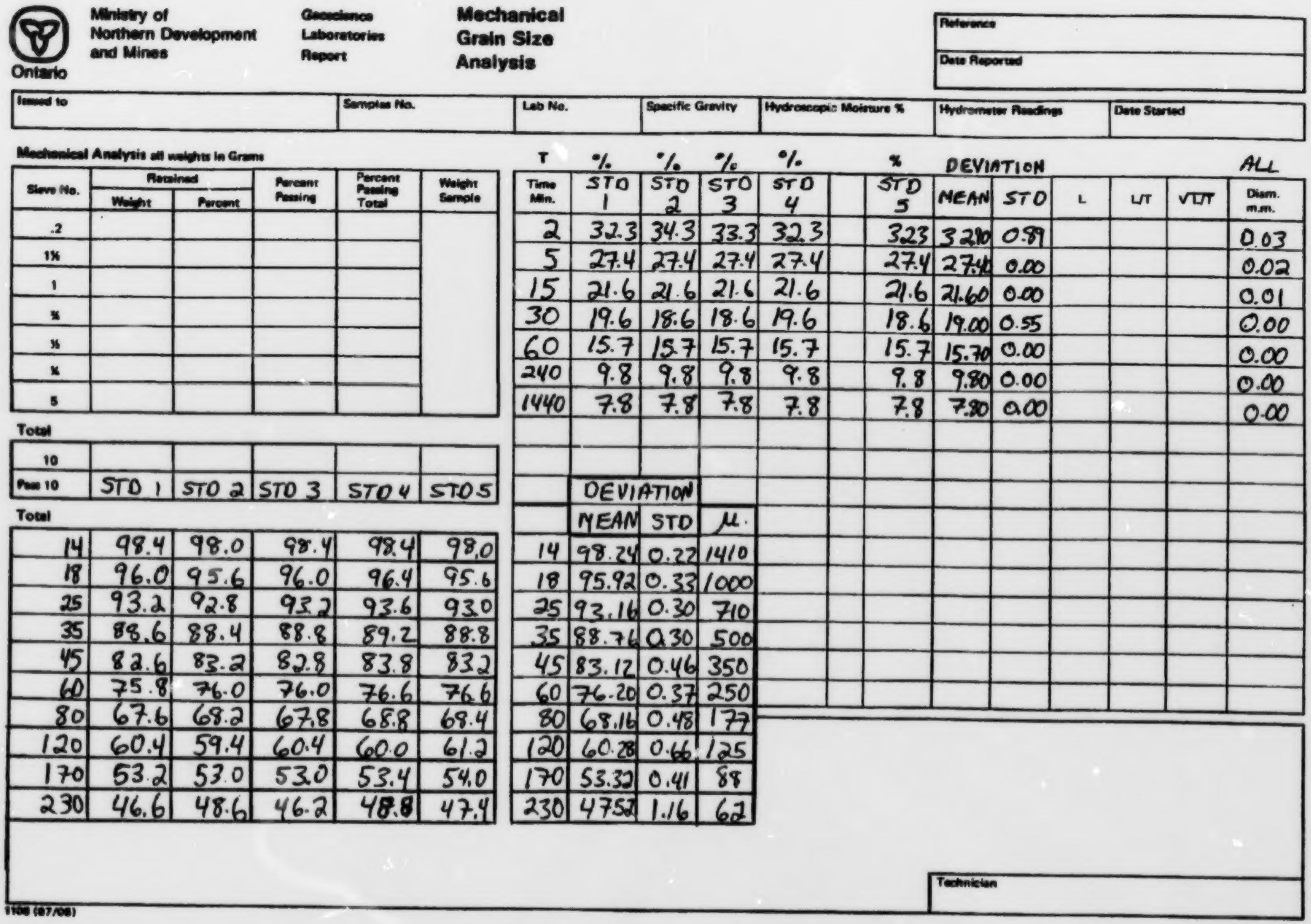
TABLE GSA2. VALUES OF K FOR USE IN FORMULA FOR COMPUTING DIAMETER OF PARTICLE IN HYDROMETER ANALYSIS

Temp. °C	Specific Gravity of Soil Particles								
	2.45	**2.50**	**2.55**	**2.60**	**2.65**	**2.70**	**2.75**	**2.80**	**2.85**
16	0.01531	0.01505	0.01481	0.01457	0.01435	0.01414	0.01394	0.01374	0.01356
17	0.01511	0.01486	0.01462	0.01439	0.01417	0.01396	0.01376	0.01356	0.01338
18	0.01492	0.01467	0.01443	0.01421	0.01399	0.01378	0.01359	0.01339	0.01321
19	0.01474	0.01449	0.01425	0.01403	0.01382	0.01361	0.01342	0.01323	0.01305
20	0.01456	0.01431	0.01408	0.01386	0.01365	0.01344	0.01325	0.01307	0.01239
21	0.01438	0.01414	0.01391	0.01369	0.01348	0.01328	0.01309	0.01391	0.01273
22	0.01421	0.01397	0.01374	0.01353	0.01332	0.01312	0.01294	0.01276	0.01258
23	0.01404	0.01381	0.01358	0.01337	0.01317	0.01297	0.01279	0.01261	0.01243
24	0.01388	0.01365	0.01342	0.01321	0.01301	0.01282	0.01264	0.01246	0.01229
25	0.01372	0.01349	0.01327	0.01306	0.01286	0.01267	0.01249	0.01232	0.01215
26	0.01357	0.01334	0.01312	0.01291	0.01272	0.01253	0.01235	0.01218	0.01201
27	0.01342	0.01319	0.01297	0.01227	0.01258	0.01239	0.01221	0.01204	0.01188
28	0.01327	0.01304	0.01283	0.01264	0.01244	0.01225	0.01208	0.01191	0.01175
29	0.01312	0.01290	0.01269	0.01249	0.01230	0.01212	0.01195	0.01178	0.01162
30	0.01298	0.01276	0.01256	0.01236	0.01217	0.01199	0.01182	0.01165	0.01149

TABLE GSA3. EFFECTIVE DEPTH BASED ON HYDROMETER AND ON CYLINDER OF SPECIFIED SIZES.

HYDROMETR 152H

Hydrometer Reading	Effective L (cm)	Hydrometer Reading	Effective L (cm)
0	16.3	34	10.7
1	16.1	35	10.6
2	16.0	36	10.4
3	15.8	37	10.2
4	15.6	38	10.1
5	15.5	39	9.9
6	15.3	40	9.7
7	15.2	41	9.6
8	15.0	42	9.4
9	14.8	43	9.2
10	14.7	44	9.1
11	14.5	45	8.9
12	14.3	46	8.8
13	14.2	47	8.6
14	14.0	48	8.4
15	13.8	49	8.3
16	13.7	50	8.1
17	13.5	51	7.9
18	13.3	52	7.8
19	13.2	53	7.6
20	13.0	54	7.4
21	12.9	55	7.3
22	12.7	56	7.1
23	12.5	57	7.0
24	12.4	58	6.8
25	12.2	59	6.6
26	12.0	60	6.5
27	11.9	61	6.4
28	11.7	62	6.3
29	11.5	63	6.1
30	11.4	64	5.9
31	11.2	65	5.8
32	11.1	66	5.6
33	10.9	67	5.5



Ontario

Ministry of
Northern Development
and Mines

Geoscience
Laboratories
Report

**Mechanical
Grain Size
Analysis**

Reference	
Date Reported	

Issued to	Samples No.	Lab No.	Specific Gravity	Hydroscopic Moisture %	Hydrometer Readings	Date Started

Mechanical Analysis all weights in Grams

Sieve No.	Retained		Percent Passing	Percent Passing Total	Weight Sample
	Weight	Percent			
.2					
1½					
1					
¾					
½					
⅜					
5					

Total

10					
Pass 10	STD 1	STD 2	STD 3	STD 4	STD 5

Total

14	98.4	98.0	98.4	98.4	98.0
18	96.0	95.6	96.0	96.4	95.6
25	93.2	92.8	93.2	93.6	93.0
35	88.6	88.4	88.8	89.2	88.8
45	82.6	83.2	82.8	83.8	83.2
60	75.8	76.0	76.0	76.6	76.6
80	67.6	68.2	67.8	68.8	68.4
120	60.4	59.4	60.4	60.0	61.2
170	53.2	53.0	53.0	53.4	54.0
230	46.6	48.6	46.2	48.8	47.4

T	%	%	%	%		%	DEVIATION					ALL
Time Min.	STD 1	STD 2	STD 3	STD 4		STD 5	MEAN	STD	L	L/T	√L/T	Diam. m.m.
2	32.3	34.3	33.3	32.3		32.3	32.90	0.89				0.03
5	27.4	27.4	27.4	27.4		27.4	27.40	0.00				0.02
15	21.6	21.6	21.6	21.6		21.6	21.60	0.00				0.01
30	19.6	18.6	18.6	19.6		18.6	19.00	0.55				0.00
60	15.7	15.7	15.7	15.7		15.7	15.70	0.00				0.00
240	9.8	9.8	9.8	9.8		9.8	9.80	0.00				0.00
1440	7.8	7.8	7.8	7.8		7.8	7.80	0.00				0.00

	DEVIATION		
	MEAN	STD	μ.
14	98.24	0.22	1410
18	95.92	0.33	1000
25	93.16	0.30	710
35	88.76	0.30	500
45	83.12	0.46	350
60	76.20	0.37	250
80	68.16	0.48	177
120	60.28	0.66	125
170	53.32	0.41	88
230	47.52	1.16	62

Technician

1106 (87/08)

Figure GSA5.

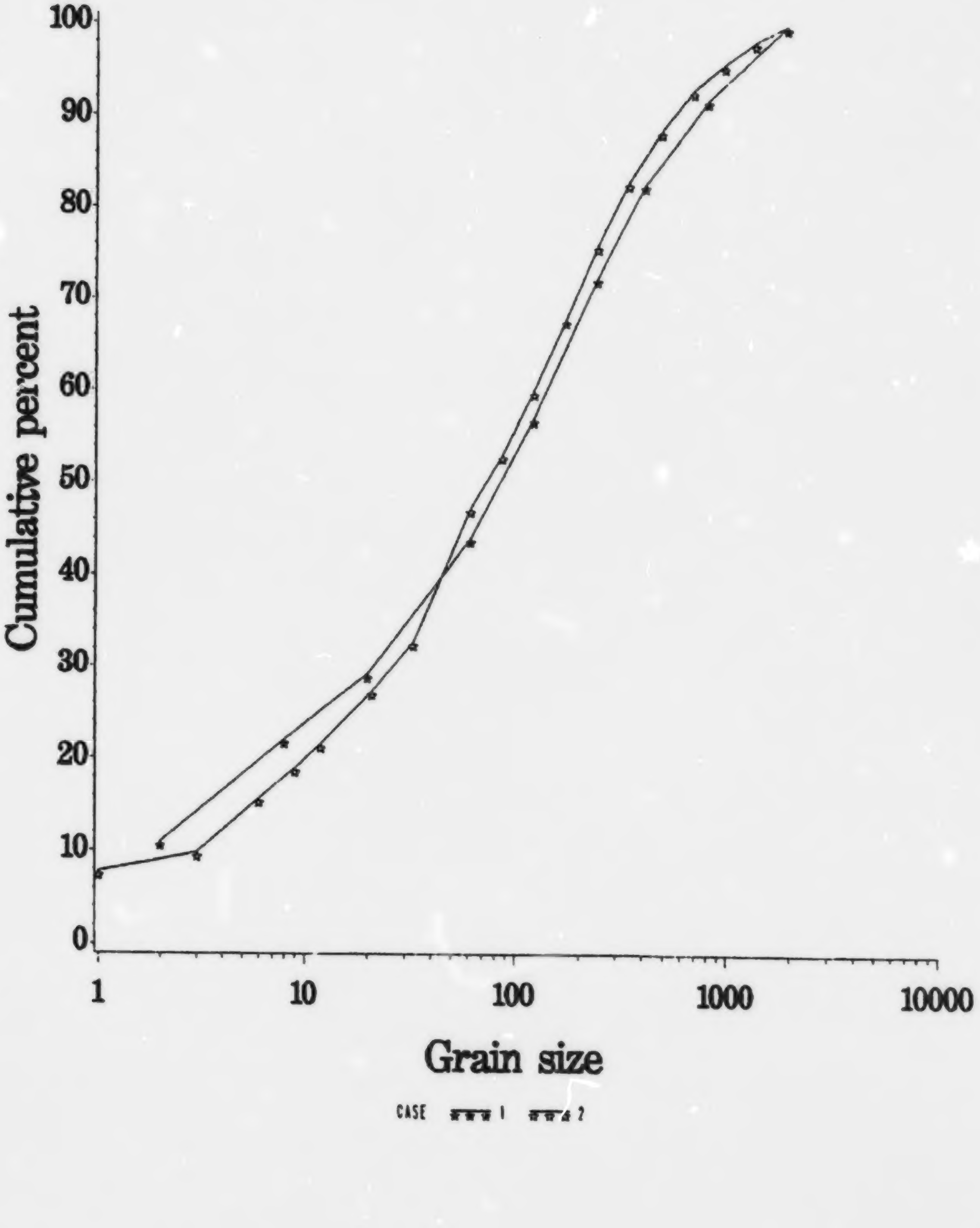


Figure GSA1. Grain-size analysis.: comparison of CLOGS (case 2) and BARRINGER (case 1).

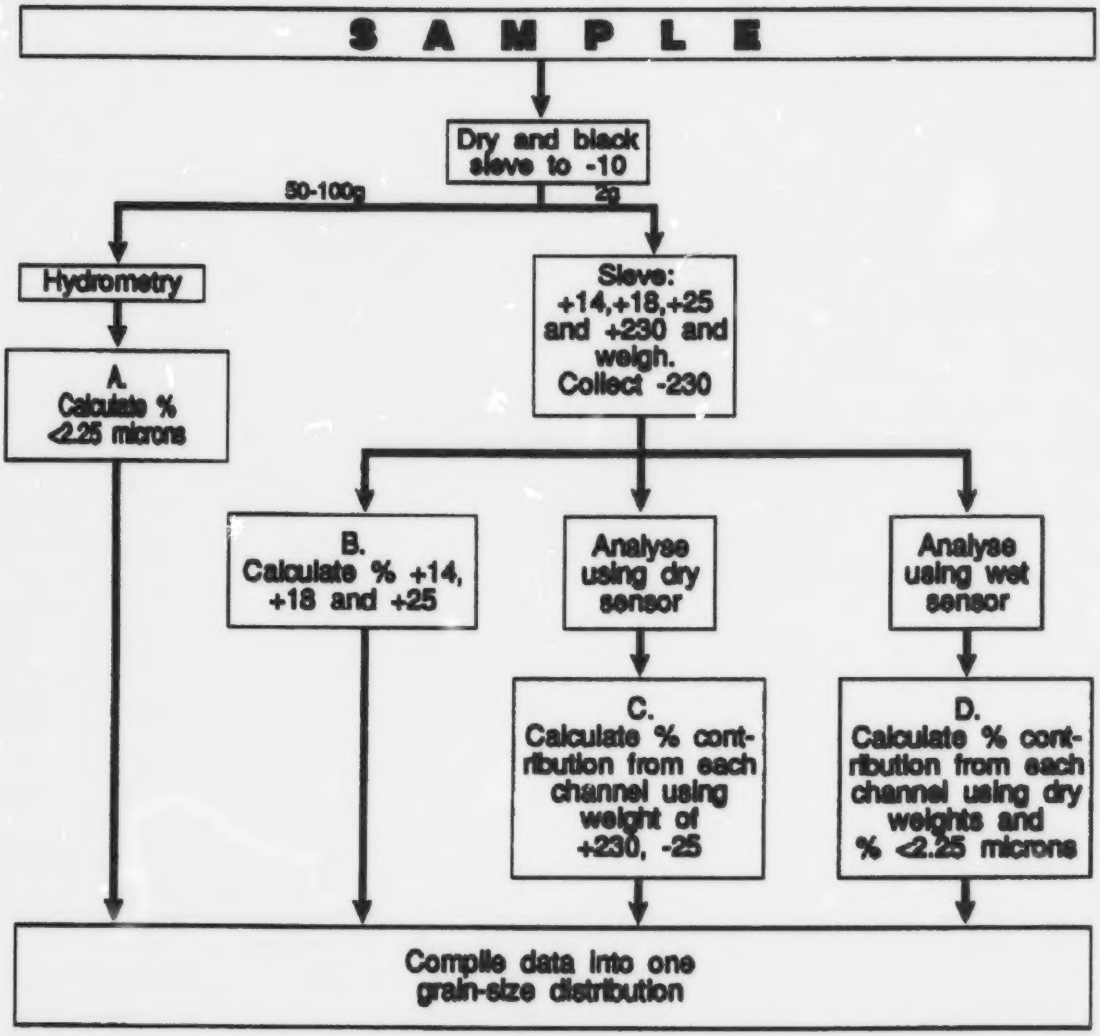

SAMPLE
Dry and black sieve to -10
50-100g
2g
Hydrometry
A. Calculate % <2.25 microns
Sieve: +14,+18,+25 and +230 and weigh. Collect -230
B. Calculate % +14, +18 and +25
Analyse using dry sensor
Analyse using wet sensor
C. Calculate % contribution from each channel using weight of +230, -25
D. Calculate % contribution from each channel using dry weights and % <2.25 microns
Compile data into one grain-size distribution

Figure GSA2. Flow chart for grain-size distribution calculation.

METHOD 2

GRAIN-SIZE ANALYSIS BY PARTICLE SIZING

This method involves the use of both modified ASTM methods and the Hiac Ryco particle sizing system. It is best applied to the determination of particle sizes for samples which are sandy, or where specific information is required about particle sizes between 2 and 700 microns. Automated grain-size analysis is not suited for routine application as a substitute for ASTM techniques for clay-rich samples.

Method:

The method consists of the following techniques:

1. Sample preparation - samples are dried and clumps of particles are broken down using a soil breaker
2. Separation of soil particles - the sample is sieved to -10 mesh, and wet sieved in the presence of a deflocculant (See previous ASTM D422-72 method) using a 14, 18, 25, and 230 sieve.
3. Calculation of results - a program is used to compile the data into an ASCII MS-DOS file, which is then reported to the geologist.

Apparatus:

- Sieves
- Soil breaker
- Mortar and rubber pestle
- Grain-size analysis system
- Hydrometer cylinders and hydrometer
- Thermometer

Reagents:

- Sodium hexametaphosphate (See previous ASTM D422-72 method for preparation instructions - Page MS4-3)

Procedure:

1. Preparation of sample

The distribution of particle sizes coarser than 710 microns (retained on No. 25 sieve) is determined by wet sieving. The distribution of particles coarser than 62 microns, but finer than 710 microns is determined using a particle size analysis system equipped with dry sensor. The particle size distribution in the fraction finer in grain size than 62 microns but coarser than 2.25 microns is determined using the particle size analysis instrument equipped with a wet sensor. The particle size distribution in the fraction finer than 2.25 microns is determined by conventional hydrometry.

1.1. Upon receipt, samples are place in drying cupboards for a week.

1.2. The sample is broken in a soil breaker, rolled, and about 50 g of the -10 sieve fraction is retained for analysis.

1.3. A 2 g sub-sample consisting of a representative fraction of the -10 mesh fraction is weighed and placed in a 250 ml jar, and 20 ml of a dispersant is added (a solution of sodium hexamethaphosphate in distilled water - 40 g per liter).

1.4. The -10 mesh fraction in the dispersant is wet-sieved through -14, -18, -25, and -230 sieves. Care is taken to wash any fine material through the sieve using a small amount of distilled water. No more than 200 ml of distilled water should be used. Particles resting on the four sieves (+14, +18, +25, and +230) are washed onto filter papers, dried in the oven at 110°C, and then weighed to 0.001 g. The -230 mesh particulates in the dispersant are poured into the original 250 ml jar, and any residual particles are washed out. The suspension is made up to 250 ml.

1.5. As outlined below the +230 fraction is analyzed using the dry sensor on the particle size analysis system, while the -230 fraction is analyzed using the wet sensor.

2. Calibration of the system

2.1. The main control unit is switched on at the back and allowed to warm up for half an hour before calibration.

2.2. A calibration must be established for the 32 channels of this system for both the wet and dry sensor. Once this calibration is completed, it can be used repeatedly, the only precaution routinely needed is to check that the channel thresholds have not drifted away from those values listed in the original calibration. When switching from the wet to the dry sensing modes, it is necessary to completely change these settings. To view the thresholds of each channel, the special function key is used, and the number of the channel is entered on the keypad (e.g. 01 for channel number 1, etc.).

2.3. The system is configured to use calibration No. 3 for the dry sensor and No. 2 for the wet sensor. A linear relationship exists between the threshold voltage of the sensor and the size of the particle, from which the millivoltage corresponding to a particular size can be established. These thresholds are kept constant for every analysis performed on the particular sensor.

3. Operation of the computer and processor

3.1. The instrument runs under the control of an IBM-PC AT clone equipped with an EGA card, monitor, math co-processor, and an extra serial port. The system runs a program called PDAS directly from the DOS COMMAND shell. Operations are explained directly by means of help menus for each function selected. Run mode parameters are selected as each run is set-up.

4. Analysis using the dry sensor

A Hiac Royco (Pacific Instruments) particle size analysis system is used to determine the grain size distribution in the solid fraction (+230, -25). Detailed instructions regarding the calibration of the instrument are presented earlier in this section. Specific attention is drawn to the following points.

4.1. A sample consisting of about 200,000 particles is introduced into the feeder chute, such that no more than 500 particles pass the sensor in each second of operation. The distribution of particle sizes is registered in 32 channels with preset size intervals.

4.2. Care must be taken not to saturate or block the sensor. Saturation may result in chains of particles being counted as single large particles. Too rapid throughput may cause the sensor to become blocked. Under no circumstances must particles larger than 25 mesh be introduced into the sensor.

4.3. Each sample should be run in duplicate. The average of the data from each analysis is used.

5. Analysis using the wet sensor

The wet sensor is used to determine the distribution of -230 mesh particles in a solution containing dispersant. As this instrument is equipped with a threshold sensor, the smallest particles which it can count are 2.25 microns in size. Specific attention is drawn to the following requirements:

5.1. The sensor must be cleaned with alcohol, micro solution and water before operation. Between samples, the sensor should be cleaned with distilled water.

5.2. The concentration limit of the sensor is dependent on the grain-size of the sample. Very dilute solutions must be used. This can be achieved by taking 1 ml of the sample solution (250 ml containing up to 2 g of sample), and making up to one liter.

5.3. Analyses should be conducted in duplicate.

6. Particle size distribution data from the sensors

Data are stored at the end of each run in a job file; two files are maintained for each job - one for each sensor. Once both wet and dry runs are completed, the ASCII translation option is invoked to create ASCII files from the PDAS data sets; this is done sequentially for each sample and standard. The ASCII files are saved on floppy disk, and the original PDAS data file is deleted from the system.

7. Analysis of the clay fraction by hydrometry

A sample of soil passing No. 10 sieve weighing 50 g (for clay-rich soils) or 100 g (for sandy soils) is allowed to soak overnight in a solution of the dispersant (125 ml). The soil and water are then transferred into a mixer for 1 minute, and washed into a graduated cylinder. The cylinder is filled to the 100 ml mark with distilled water. The covered cylinder is inverted repeatedly for 1 minute before commencing the readings, and readings are then taken after 1 hr, 2 hrs, 3 hrs., and 4 hrs. The hydrometer scale should be read at the top of the meniscus. A working temperature of 23°C is assumed, but if very different, then a correction is applied in the calculation (Table GSA2).

8. Grain Size Calculations

The calculation of grain-size distribution follows the flow chart shown in Figure GSA2. The percentage of particles of size less than 2.25 microns is determined using the following calculation:

8.1. Percentage of soil in suspension (SS%)

$$SS = \frac{R\, x\, a}{W}\ x\ 100\%$$

where, SS = percentage of soil remaining in suspension at the level at which the hydrometer measures the density of the suspension.
R = corrected hydrometer reading
a = correction factor to be applied for the reading of the hydrometer (See Table GSA4)
W = oven-dry weight in grams of soil dispersed and used for the hydrometer readings

TABLE GSA4. CORRECTION FACTOR (a)

Specific Gravity (g/cc.)	Correction Factor (a)
2.95	0.94
2.90	0.95
2.85	0.96
2.80	0.97
2.75	0.98
2.70	0.99
2.65	1.00
2.60	1.01
2.55	1.02
2.50	1.03
2.45	1.05

8.2. Diameter of soil particles (D)

$$D = K\, \frac{1}{L/T}$$

where, D = diameter of particle (mm)
K = constant depending on the temperature of the suspension and the specific gravity of the soil particles (Table GSA2)
L = distance from the surface of the suspension to the level at which the density of the suspension is known (cm).
T = interval of time from beginning of sedimentation to the taking of the reading (min.).

8.3. The percentage of particles of size 2.25 microns or less (SL) is calculated from a plot of percentage of soil in suspension against the diameter of the soil particles.

9. The percentage of particles with sizes between 710 and 2000 microns.

The weight percent of sample from the +14, +18, and +25 sieves can be used to calculate the weight percent contribution in each of these grain-size intervals (i.e A = wt. retained on No.14/100, etc.).

10. The percentage of particles (PL%) with sizes between 2.25 and 65 microns is determined by

$$PL = \frac{(W - (A + B + C + D) - SL)}{100}$$

where, PL = percentage of particles being analysed by the wet sensor
W = original weight of sample in grams prepared for grain-size analysis (not hydrometry).
A,B,C, and
D = percentage of sample retained on No. 14, 18, 25, and 230 sieves, respectively (i.e. weight/100).
SL = percentage of particles with grain sizes less than 2.25 microns (determined from hydrometry).

The contribution of particles in each grain-size interval determined by the wet sensor is then calculated by multiplying the percentage in that channel (for each of the 32 channels) by the overall percentage of particles analyzed by this sensor (PL).

11. The percentage of particles with sizes between 65 and 710 microns.

This is determined by multiplying the count in each of the 32 channels by the percentage contribution (by weight) made by the particles falling in this grain-size interval (e.g. D).

12. Recalculation of data

Hydrometry and sieve data for each sample are entered into an ASCII file using a GWBASIC program (GRAIN.ANY). This information is then combined with the data from the ASCII files for the wet and dry sensors using a program which generates an ASCII file and report.

Quality Control:

Analysis of the in-house GLOGS soil standard should accompany each batch of samples. Hydrometry determinations on the GLOGS standard are made without using stock material, as the amount of this standard used in a hydrometry determination would be 50 g.

The method produces a slightly different gradation curve compared to the conventional ASTM method.

Productivity:

A technician should be able to complete 40 samples per week with the automatic system.

ATTERBERG LIMITS (ASTM D423-66)

Introduction:

The Atterberg Limits represent the liquid and plastic limits of a soil, which in turn are used in the classification.

The Atterberg limits are frequently used in specifications for controlling the type of soil used in a variety of engineering projects.

Procedure:

1.1. The soil sample is placed on a glass plate and thoroughly mixed with distilled water. Part of the soil mixture is then placed in the Liquid Limit device, which consists of a brass cup and carriage. With a spatula, soil is leveled and trimmed to a depth of 1 cm at the point of maximum thickness. With the use of a grooving tool, the soil is divided along the diameter through the center line of the cup.

1.2. By turning the crank, the cup is lifted and dropped at a rate of two revolutions per second until the two halves of the soil cake come into contact at the bottom of the groove along a distance of 1.3 cm. The number of drops needed to close the groove for a distance of 1.3 cm is recorded.

1.3. Part of the soil that flowed together is taken and placed in a container; the wet weight is recorded, and then the soil is oven dried to 110°C. The sample is re-weighed, and the dry weight is recorded. This procedure is duplicated. The procedure is repeated until the sample acquires a consistency that will require 25(+/-10) drops to close the groove.

2. Calculations

$$L1 = Wt.\ water \times 100 \times \frac{k}{Wt.\ dry\ soil}$$

where, k = constant depending on the number of blows (See Table ATT1)

L1 = liquid limit.

$$P1 = Wt.\ water \times \frac{100}{Wt.\ dry\ soil}$$

where, P1 = plastic limit.

TABLE ATT1. CONSTANTS USED IN THE DETERMINATION OF ATTERBERG LIMITS

No. Blows	k
10	0.906
11	0.913
12	0.920
13	0.927
14	0.934
15	0.941
16	0.948
17	0.955
18	0.961
19	0.968
20	0.974
21	0.979
22	0.985
23	0.990
24	0.995
25	1.000
26	1.005
27	1.009
28	1.014
29	1.018
30	1.022
31	1.026
32	1.030
33	1.034
34	1.038
35	1.041
36	1.044
37	1.047

Quality Control:

The GLOGS soil standard is analyzed on a regular basis and the results are compared with in-house accepted values for this standard (Table ATT2).

Productivity:

A technician should be able to complete 40 samples per day for non-clay material and 10 samples per day for clay-rich soils.

EXAMPLE REPORT FOR STANDARD LIQUID

			LIMIT							
SAMPLE NO.	CODE	PLASTIC LIMIT	NO. OF DROPS	FIRST TRIAL	NO. OF DROPS	SECOND TRIAL	NO. OF DROPS	THIRD TRIAL		LIMIT
# OF CONTAINER⟶		1		2		3		4		
STANDARD A	Wet Wt. Soil & Can	21.95	21	32.33	23	34.54	26	41.12	15	Liquid
B	Dry Wt. Soil & Can	21.07		29.82		37.78		37.58	12	Plastic
C	Wt. Moisture	0.88		2.51		2.76		3.54	3	Plastic
D	Wt. Can	13.74		13.26		13.41		13.63		
E	Wt. Dry Soil	7.33		16.56		18.37		23.95		
F	% Moisture	12.01		15.16		15.02		14.78		
G	Plastic or Liquid Limit	12		15		15		15		

C = A - B

E = B - D

F = C/E x 100

G = rounded value of F

G = F x factor based on No. of blows (see Table)

Plasticity index = Liquid limit - Plastic limit

Table ATT2.

SEPARATION OF MINERALS USING HEAVY LIQUIDS

Introduction:

Heavy liquids are used to fractionate mineral phases from each other, by differentiating the minerals based on their inherent density. Separated minerals may then be weighed and/or analyzed by conventional geochemical techniques.

Mineral separations using heavy liquids require that the density of the liquid is such that the mineral to be separated either sinks or floats in the liquid while the rest of the sample does the opposite.

Heavy liquids most widely used in the laboratory are shown in Table HLS1.

TABLE HLS1. HEAVY LIQUIDS.

Liquid	Density g/cc at 20°C
Bromoform	2.89
Tetrabromoethane	2.964
Methyl iodide	3.325
Sodium polytungstate	Adjustable up to 2.9

NOTE: The first three chemicals are light sensitive, and should be stored in dark-coloured containers.

Sodium polytungstate will tend to crystallize if the solution is too concentrated.

Safety advisory:

1. The organic heavy liquids are toxic and should be handled with great caution. Do not open bottles, or use outside of a well vented hood. These liquids are known carcinogens. Staff should read the pertinent MSDS sheets.
2. Ingestion and contact with skin must be avoided.
3. The fumes from these liquids are heavier than air. Use down draft hood if possible.

Procedure:

1. Preparing liquids for use

Lowering or increasing (for sodium polytungstate only) the densities of heavy liquids:

The densities of the first three liquids (Table HLS1) can be lowered by diluting with a number of miscible organic solvents, including: benzene, carbon tetrachloride, acetone, and alcohols.

Sodium polytungstate is soluble in water at room temperature. Solutions should be stored in air-tight containers to prevent evaporation of water.

2. Recovery or cleaning of organic heavy liquids

Depending on the nature of the chemical used to dilute the heavy liquid, the organic heavy liquid may be recovered from diluted mixtures by fractional distillation at reduced pressure (for methyl iodide), or simply by evaporation in a vented hood.

When acetone is used, it may be completely removed by streaming water through the diluted heavy liquid until a suitable density marker (specific gravity block) or mineral fragment placed in the liquid floats. The purified liquid is then separated from the excess water and finally dehydrated by shaking with calcium chloride followed by filtration.

3. Separation procedure

Separations may be made at any particle size down to a limit of about 10 microns. Below 150 microns, a centrifuge becomes necessary to accelerate the settling rates of the fine particles.

The weight of material processed may vary from a few milligrams to 200-300 g.

The sample must be thoroughly cleaned and free of all clay particles. This may be done with the aid of a dispersing agent such as sodium hexametaphosphate or sodium silicate, after which the sample is dried and dry-sieved to obtain the size of grains required for separation (usually -60 +120 mesh).

3.1. Take a portion of the sample (-60 +120 mesh) and weigh a minimum of 1 g to within 0.01 g.

3.2. Transfer the sample into a glass separating funnel (fitted with stopper) filled with 200 ml of heavy liquid.

3.3. Gently stir the grains into the liquid to ensure complete wetting. Grains with densities greater than the density of the liquid will settle to the bottom of the funnel (heavy minerals); light minerals will float on the surface of the liquid. During the separation, stir the grains 3-4 times, depending on the quantity of material used.

3.4. Drain the heavy minerals into a filter paper (Whatman -4 qualitative).

3.5. Wash the collected minerals 3 or more times with a suitable solvent (acetone) to remove all trace of heavy liquid.

3.6. Dry the sample in an 110°C oven for 3-5 days.

3.7. Weigh and dry the heavy minerals collected (to 0.001 g).

3.8. Remove all magnetic minerals from the sieve.

3.9. Weigh the non-magnetic fraction to 0.001 g.

4. Calculations

$$PH = WH \times \frac{100}{W}$$

where, PH = percentage of heavy minerals in the sample,
WH = weight of heavy minerals in grams, and
W = weight of material used in grams.

$$PM = (WH - WN) \times \frac{100}{W}$$

where, PM = percentage of magnetics in the sample, and
WN = weight of non-magnetics.

Productivity:

A technician should be able to complete 25 samples over a period of 2 days.

MINERAL SEPARATION USING THE FRANTZ MAGNETIC SEPARATOR

Introduction:

Many different minerals may be separated from each other on the basis of their magnetic susceptibility. For practical purposes minerals can classed into three groups depending on their magnetic properties:

1. Ferromagnetic: the most magnetic minerals eg magnetite. These are actually strongly paramagnetic minerals.
2. Paramagnetic: most minerals are paramagnetic and are attracted by a magnetic field.
3. Diamagnetic: weakly magnetic minerals repelled by the magnetic field eg quartz, feldspar.

The Frantz magnetic barrier separator consists of a vibrating inclined chute, partly divided along its length, along which minerals are fed; specially designed pole pieces exert a strong magnetic barrier field along the centre of this chute. Mineral separation takes place in the middle of the chute by balancing magnetic forces on each mineral against the gravitational forces. The divider separates the two mineral streams directing them into bins at the end of the chute.

The vibrating chute has a forward inclination which controls the speed at which minerals move down the chute. This is normally set at about 20 to 30 degrees. The chute also has a side inclination the setting of which controls the gravitational force on the mineral grains. This is usually set at about 15 degrees for the first few passes but may be increased to around 60 degrees in the later stages of a mineral separation. The strength of the barrier field is controlled by a rheostat; magnetic separations separate the strongly magnetic minerals first from the sample and proceed in order of decreasing magnetic susceptibility. Therefore, the barrier field is initially very weak so that the ferromagnetic and strongly paramagnetic minerals can be removed.

As the mineral stream enters the middle of the chute the gravitational forces on the mineral mixture will act so as to impel the mineral grains toward the lower edge of the chute. As they travel through the centre of the chute they interact with the magnetic barrier field. Those minerals less magnetic than the field will carry on through this region towards the lower edge of the chute; those minerals with a magnetic force equal to or greater than the barrier field are deflected by it and stay on the upper side of the chute. As the strength of the barrier field is increased it is able to deflect minerals with weaker and weaker susceptibilities and thus separate minerals on the basis of their magnetic properties. The range of magnetic susceptibility of various minerals is given by Rosenblum (1958), Flinter (1959) and Hutchison (1974). Note that the currents given by these authors are for the isodynamic separator; the newer barrier separator uses much lower currents.

For ferromagnetic minerals the residual magnetic field is still too strong for successful separation of these minerals. The Frantz low field control can be used to separate these minerals as it reverses the direction of the current to establish a hysteresis loop that reduces the magnetic field to zero. When separating paramagnetic minerals, material is fed into the inner channel of the chute which has a side inclination such that gravitational forces push the feed into the other outer channel. For diamagnetic separations this is reversed: the feed is in the outer channel and the side inclination is toward the pole pieces.

Safety advisory:

1. The high magnetic fields generated by the pole pieces may have a harmful effect on pacemakers and hearing aids. These fields will also cause damage to watches, calculators, magnetic disks, bank and security cards, etc.

Method:

1. Sample preparation - the sample should be washed to remove fine powders which could alter the magnetic properties of the mineral to which it is adhering and also clog the separator. Sizing is also important; while the best grain size to work with will depend on the rock, the most common size range used is -100 +140. Finer sizes may be used if the proportion of composite mineral grains is unacceptably high. Finally a hand magnet is passed over the sample to remove the ferromagnetic minerals which can clog the flow of material in the chute unless removed.

2. Mineral separation - the material is placed in the feed hopper and using an appropriate feed rate is fed onto the vibrating chute. The fastest way to proceed is to divide the material by half during

each pass making sure that the mineral of interest is entirely in one of the halves. The magnetic range necessary for the separation of that mineral will soon be arrived at. At any stage if the volume of material is sufficiently small (<50 ml) heavy liquids may be used to further concentrate the mineral required.

The final stages of separation will take place at high side inclinations and changes in the magnetic field between passes will be very small. The most important point to remember is that each rock is different and that there are no set procedures to follow; trial passes are always necessary to see how a mineral mixture reacts to different settings of the magnetic field, feed rate and side slope.

Apparatus:

- Magnetic separator
- Binocular microscope
- Clean paper to cover the working surfaces to prevent contamination and recover mineral mixtures when they are split
- Hand magnet to remove ferromagnetic minerals
- Plastic vials to store the various mineral fractions
- Compressed air, brushes etc. for cleaning the instrument
- Titanium-tipped tweezers

Reagents:

None required.

Procedures:

1.1. The rock sample is reduced to its component mineral grains by crushing it in a jaw crusher followed by pulverization in a mill. In the Braun pulverizer, several passes, reducing the gap between the plates each time, are necessary to avoid too much fine material. A roll mill, if available, produces a better result, as the crushing action here as opposed to the ripping action of the former results in more liberated grains.

1.2. A hand magnet should be passed over the sample at this stage to remove iron filings and magnetite which could stain the other minerals. These should be saved in case they are needed at a later time. The hand magnet should be in a plastic bag so that the poles are not coated by the magnetic particles; alternatively, an enclosed plunger-type magnet may be used.

1.3. The sample is placed in a deep container and washed in water to remove the rock flour. Swirl the water through the sample and let stand still for 15-20 s before decanting the water. Be careful not to lose micas when decanting; they often float on the water surface as a result of surface tension effects. Washing should continue until the decanted water is clear. The final rinse should be with acetone or alcohol to speed drying. Dry the sample under a heat lamp or in a warm oven overnight.

1.4. When dry, sieve the sample using clean nylon cloth sieves. The usual size is -100 +140 mesh but the grain size of the rock will be the major factor in deciding what size should be used. The sieve clothes can be placed over the mouth of a 500 ml jar attached with rubber bands, containing approx 100 ml sample. Shake the jar until no more grains pass through. When about 50 ml of the desired size range is available start the magnetic separation and complete the sieving of the rest of the sample later. Before putting the sample in the feed hopper pass the hand magnet over it once more to remove any leftover magnetic grains.

1.5. The magnetic separator should be thoroughly cleaned prior to starting the separation. Brush the pole pieces carefully, as well as the trough behind them which often contains minerals from the previous separation. Stand the pole pieces vertically and brush them out. Sample cups, the feed hopper,and other surfaces in contact with the sample should be wiped with tissue paper soaked in alcohol. The chute must not be wiped or touched with the fingers; if it is greasy, wash it in detergent and hot water and let it dry. Otherwise, blow it clean and reassemble the pieces.

1.6. The initial settings are 10° side slope, 20° forward inclination. The feed is into the inner channel for the separation of paramagnetic minerals and the side slope is forward, away from the pole pieces. The chute is angled so that the top end is under the pole pieces and the bottom end outside of them. The gate at the bottom end of the feed hopper and the vibration of the hopper are adjusted so that flow rates are about 5 ml per minute; in the final stages a feed rate of less than 1 ml/min is appropriate. The vibration of the chute is also adjusted so that the travel time of grains from one end to the other is about 30 s.

1.7. The initial magnetic setting is dependant on the sample but 0.1Å is normally used. The current is increased on successive passes. Once the more magnetic minerals which could clog up the chute have been removed the sample may be run at a current high enough to divide it into two equal fractions with the mineral of interest entirely in one. This will speed up processing particularly if the sample is large. Also relatively high flow rates can be used as the deterioration in the separating ability of the Frantz is not of great concern at this stage. The sample volume is halved on each successive pass until the mineral of interest is concentrated. Note that in the separation of diamagnetic minerals the feed is into the outer channel of the chute which is sloped in toward the pole pieces.

1.8. The final stages of the separation take place at much slower feed rates so that the separation is precise and entrainment of grains does not occur. The side slope is also increased to about 60° so that the gravitational component is increased with a corresponding increase in the magnetic field. This allows for a more precise separation as small differences in magnetic susceptibility can now be exploited. Special feed troughs are available so that the grains do not spill and the feed rate is narrowly controlled.

1.9. The settings in these final stages are a matter of trial and error. Frequent checking of the separated products using the binocular microscope, grain mounts and the X-ray diffractometer will help control the quality of the separation.

1.10. Often the range of magnetic properties in the mineral being separated are such that it does come clean at a relatively narrow magnetic range and therefore the final product will contain some impurities. Most of these may be removed by heavy liquid separation.

1.11. The final product will still contain a few impurities which will have to be removed by hand-picking under a binocular microscope.

Quality Control:

A grain mount should be made of the final product to demonstrate its purity (refer to the section on optical mineralogy, page M9-1).

Productivity:

Variable. Dependant on the volume and the difficulty of the separation.

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ROCK AND MINERAL IDENTIFICATION FOR PROSPECTORS AND GEOLOGISTS

Introduction:

The identification of minerals is an essential first step in the classification of rock samples (see Vol. I, Chapter 15). The initial examination of a rock may be carried out with the naked eye, with a hand lens, or with a stereo microscope. Sufficient information may be obtained at this stage for a preliminary identification which can be confirmed using grain mounts or thin sections in the optical microscope, XRD, or other more advanced techniques.

Some of the tests and observations which may be used by the mineralogist in a visual identification are listed here together with other information. This information may be incorporated into a report for the geologist or prospector.

Visual Examination

Hardness:

One of the most useful tests in mineralogy is the simple scratch test, comparing the ease of leaving a scratch mark on the mineral. A series of 10 minerals were used by Mohs to develop a hardness scale in a range of 1 to 10. Each mineral in the scale can be scratched by the one above it. The scale intervals are approximately equal except that diamond is about 30 times harder than corundum.

Most minerals have a hardness of less than 7. Minerals with a hardness of up to 2.5 can be scratched with a fingernail; hardness of up to 3 can be tested with a copper coin; a knife can scratch minerals with hardness of less than 5.5; a porcelain streak plate can scratch minerals with hardness of less than 6.5; a steel file will scratch minerals with hardness of less than 7.

Hardness is a measure of the strength of the bonding of the atoms in a crystal, and consequently can vary depending on the direction in which it is scratched. For example, kyanite forms narrow bladed crystals which have a hardness of 4-5 along the axis, and 6-7 at right-angles to the axis.

Luster:

The appearance of the surface of a mineral in reflected light is a quality termed luster. On the basis of luster, minerals can be divided into metallics and non-metallics. Pyrite and galena have a well-developed luster. Non-metallic minerals have luster which can be described in a number of ways (e.g: vitreous - resembling glass; greasy - as if coated with a thin layer of oil; silky - resulting from fibrous aggregations of parallel crystals; adamantine - having a hard brilliant luster; pearly - resembling mother of pearl; resinous - resembling resin).

Colour:

For many minerals, colour is a reliable guide to identification. In the metallics, fresh surfaces frequently reveal quite diagnostic colours (e.g. yellow in chalcopyrite). Nonmetallics display a greater variety of colour.

Streak:

Streak is the colour of the powdered mineral. It is usually obtained by rubbing the mineral over an unglazed porcelain streak plate. Metallic minerals produce quite distinctive streaks.

Crystal Habit:

Crystals vary considerably in shape depending on rates of growth, impurities present during growth, and the nature of the host. Nevertheless, some mineral phases are often characterised by particular shapes called crystal habits. Well known terms are fibrous, acicular (needle-like), columnar, tabular, scaly, and micaceous. In addition, form names are often used such as cubic, prismatic, pyramidal, etc.

Cleavage, fracture and parting:

Many crystals break along smooth planes which are parallel to possible crystal faces. Such planes are called cleavage planes. Cleavages are repeated by the symmetry of the crystal in exactly the same way on all faces. A cleavage may often be described as perfect, good, distinct, imperfect or poor depending on its development.

Fracture refers to the shape of surfaces formed by breaking a crystal in a direction other than the cleavage. Fracture may be conchoidal, even, uneven, or hackly.

Twinned crystals:

A twinned crystal is formed of two or more individuals of the same mineral joined together according to a defined law. They may be joined as contact twins on a plane, or as penetration twins.

OPTICAL MINEROLOGY

Introduction:

Rock and mineral samples are examined under the polarizing optical microscope as thin sections or grains, to allow examination of rocks in transmitted light.

Procedures:

1. Preparation of thin sections

1.1. A small chip of rock or mineral is sampled, or a thin slice (<5 mm thick) is cut from the specimen using a diamond saw.

1.2. The chip or slice is ground flat and smooth on the surface using progressively finer abrasive, e.g. Carborundum powder, starting with 80 grade and finishing with 600 grade.

1.3. The smooth surface is cemented to a glass slide (usually 2"x1") using Canada balsam or Lakeside 70 cement.

1.4. The other surface is ground down until the rock section is 300 microns thick. Progressively finer abrasives are used as the section becomes thinner, and finishing is done with 600-grade Carborundum powder. The thickness is gauged by observing the interference colours of common minerals such as quartz or olivine.

1.5. After cleaning excess cement from the surface of the section, it may be covered with a glass slip, cemented in place with Canada balsam.

Canada balsam may be thinned with xylol to ease spreading. The mounting is done on a hot-plate which serves to drive off xylol and harden the cement.

Some poorly consolidated samples require impregnation with a cement before a section can be made. Heating the sample in Canada balsam is often sufficient.

Loose and crushed grain mounts may be made from unconsolidated sediments and loose minerals. The grains are spread on a glass slide, and immersed in Canada balsam. The mount is covered with a glass slip. For crushed grain mounts, an immersion liquid capable of supporting the cover-slip by capillary action is sufficient.

Fine grinding for the production of sections suitable for microprobe analysis is performed on a rotating lap in two stages; a cover slip is not applied. In the first stage, 6 micron diamond paste is used, and in the second step, 1 micron diamond paste is used.

2. Determination of refractive index

In a normal thin section, it is rare for the contacts between mineral phases to be vertical and for the surfaces to be smooth. If there is a difference in refractive index between the mineral and cement, the irregularities (stepping or curving of the grain margin) concentrate or scatter light by reflection and refraction. The effect is to give an impression of three-dimensional relief (high relief). If the difference in refractive index is small, the irregularities will hardly be visible, and the mineral has low relief. Relief may be observed in plane polarised light with a low or medium power objective, with the diaphragm nearly closed and with the condenser assembly lowered.

Description of relief is subjective, but can be reference to the refractive index (RI) of Canada balsam (RI = 1.537). For example, rutiles have a high relief, whereas quartz has a low relief. The Becke line test may be applied to determine whether low relief minerals have higher or lower refractive indices than Canada balsam. Under similar light conditions to those described above, low or moderate relief minerals concentrate light as a thin bright white line along their margins. This line, termed the Becke line, will move inwards or outwards if the mineral grain is brought slowly into or out of focus. The Becke line moves into the substance of higher RI, when the distance between the objective and section is increased.

A more accurate means of determining RI involves the use of loose or crushed grains of a mineral in a series of liquids of known RI. The relief of the mineral will disappear when its RI, matches that of the liquid.

A small amount of the mineral is crushed to a powder, and placed on a glass slide. The powder must be neither to fine nor too coarse as a fine powder is too hard to observe, yet a coarse powder will tend to float. A glass slide is placed on the dry powder, and the RI liquid is introduced at the margin of the coverslip using a dropper. The procedure is repeated with different RI liquids until the RI of the mineral is matched to that of the liquid. When the RI of the mineral is within 0.002 of the RI of the oil, colored Becke lines are seen.

RI liquids are obtained commercially, or can be produced in-house (Shelly, 1975).

3. Determination of birefringence

The birefringence or partial birefringence of a mineral section is determined in thin section by observing interference colours in crossed-polarised light with the diaphragm below the stage open, and using low-power objectives. The Michel-Levy colour chart presents the relationship of birefringence to the thickness of the section (horizontal lines) and interference colour (vertical lines). Figure OM1 illustrates how the chart is read. For example, a mineral with colour A and thickness B, has a birefringence, or partial birefringence of C. To perform this determination, several grains of a mineral in a thin section are cut parallel to different crystallographic directions, and hence intersect the indicatrix in different orientations. The interference colors will vary from black in sections cut parallel to the circular section to a maximum for those cut parallel to ε and ω, or X and Z. The grains with the highest interference colors will therefore be diagnostic of the birefringence. Preferred orientation in layered or banded rocks often introduces a bias in the section, and caution is required in the interpretation of the interference color.

Interference colours are normally split into orders corresponding to the amount by which two rays are out of phase. The simplest method of determining the order of the colour is to look at the edge of the mineral grain. Edges of grains which are wedge-shaped show a range of interference colours from 1st order grey at the thin edge, inwards towards progressively higher order colours. By counting the colour rings, the order of the colour in the main part of the mineral section can be determined.

In thin sections which are 30 microns thick, quartz may be used as a control on the birefringence of other phases, as it invariably shows first-order pale yellow.

3.1. Fast and slow direction: the use of accessory sensitive tint plates

The 1-wavelength plate (made of gypsum or quartz) has the thickness and orientation to produce 1st-order pink. This plate has two vibration directions in the 45° position which are marked on the plate as fast and/or slow. The accessory plates are used to increase the equivalent thickness of the thin section and to compensate for the wavelength difference produced by a mineral. This is performed by putting the mineral section in extinction (Figure OM2) thus producing two vibration directions E-W and N-S.

The stage is then rotated through 45° noting whether clockwise or anticlockwise to determine the colour produced by the mineral. Insertion of the plate is accompanied by a change in the colour. If retardation occurs (i.e. the interference colour increases), then the slow direction of the plate is parallel to the slow direction of the mineral. If compensation occurs (i.e. the interference colour decreases), then the slow direction of the plate is parallel to the fast direction of the mineral.

The fast and slow directions are partially diagnostic in the identification of mineral phases.

3.2. Interference figures, determination of optic sign, and measurement of 2V

Interference figures are obtained as follows: focus on a grain with a high-power objective, and center the grain in the field of view, center the microscope, and raise the sub-stage condenser, opening the sub-stage diaphragm. Using cross-polarised light, insert the Bertrand lens. The stage should be rotated when observing interference figures so that the pattern of the isogyres can be noted.

Interference figures indicate whether the the mineral is uniaxial or biaxial, and with the aid of the sensitive tint plate, the optic sign can be determined. 2V can be obtained on biaxial minerals. These properties can all be determined from grains cut parallel to circular sections of the uniaxial or biaxial indicatrix. Therefore, the best grains are those with the lowest interference colours (black or grey). Such grains give a uniaxial cross, or a biaxial optic-axis figure. Isotropic minerals will not produce an interference figure.

3.3. Use of accessory plates to determine optic sign

To determine the optic sign, interference figures and sensitive tint plate are used together. In uniaxial figures, the ε-vibration directions are radial to the ω direction. Insertion of the plate results in retardation or compensation in alternate quadrants. Minerals with positive ε are slow, whereas minerals with negative ε are fast. Thus, as shown in Figure OM2, the change in pattern is diagnostic of positive or negative uniaxial minerals.

In biaxial figures, the pattern of retardation and compensation in relation to the isogyres enables the positions of X,Y, and Z to be determined, and the optic sign of the mineral.

3.4. Interpretation of figures

3.4.1. Uniaxial cross interference figures (Figure OM2).

The mineral is uniaxial or biaxial with 2V close to 0°. The optic axis is approximately vertical in the section. The positive or negative character can be determined.

Off-centred figures can be used provided the centers can be seen. In these circumstances, the optic axis may be 20-30° from vertical. When the crossed isogyres move out of the field of view, there is no guarantee that the figure is not biaxial, and therefore these figures should not be used.

3.4.2. Biaxial optic-axis figures (Figure OM2)

If the middle of an isogyre remains in the centre of the field of view during rotation of the stage, the mineral is biaxial (Figure OM2). The degree of curvature of the isogyres enables 2V to be estimated. For a 2V of 90°, the isogyres remain straight during rotation. The curvature becomes large at 2V less than 20°. At 0°, the figure resembles a uniaxial cross. The positive or negative character can be determined with the tint plate (Figure OM2). If 2V is 90°, the mineral is neither positive nor negative.

If the isogyres remain in the field of view when the stage is rotated (Figure OM2), the mineral is biaxial, and the acute bisectrix is near vertical in the section. Positive or negative character can be determined, and 2V estimated when the isogyres are in the 45° position. If the isogyres barely separate, 2V is very small (less than 10°), whereas if 2V is 50° the isogyres move to the edge of the field of view.

If the isogyres move slowly out of the field of view when the stage is rotated, the mineral is biaxial, and the acute or obtuse bisectrix is near vertical. The 2V is moderately large. The optic sign cannot be determined if the bisectrix is close to vertical.

If the isogyres move quickly out of the field of view when the stage is rotated (Figure OM2), then the optic sign can be determined, but the distinction between uniaxial and biaxial is not clear-cut.

4. Crystal shape and cleavage

Shape is not a diagnostic feature in thin-section, but is a useful guide. Euhedral crystals of many minerals have characteristic shapes and habits that can aid in the identification of minerals.

Cleavage is commonly observed as a set of cracks or bands in a mineral section. Cleavage vertical to the section appears as fine cracks, but cleavage oblique to the section will produce broad dark bands. The number of cleavages, and their relative orientations and relations to the crystal faces are diagnostic features of certain mineral phases.

The extinction angle may be used to document aspects of shape and cleavage. The angle between a vibration direction and a cleavage or prominent crystal face is termed the extinction angle. If the angle is zero, the mineral has straight extinction. Extinction angles are particularly useful in the determination of plagioclase determinations.

5. Colour and pleochroism

Most mineral phases are transparent in thin section, but a few mineral phases are opaque. Colour is judged with the analyzer removed. Colour can be a useful property, but is rarely diagnostic.

Opaque minerals are best studied using a microscope fitted for reflected light work.

Anisotropic minerals frequently display variations in colour or intensity of colour when the stage is rotated in plane-polarized light, a phenomenon termed pleochroism.

6. Point counting to determine the modal mineralogy

In order to assess the relative proportions of mineral phases, it is often necessary to utilize a polarizing microscope equipped with a point counting stage. Such a stage is mounted on the rotating stage, and is capable of being moved by a finite and constant distance in either direction parallel to the cross-hairs of the microscope. At each point on the thin section or polished section (reflected light microscope), the phase is identified visually, and the stage is advanced simultaneously as the counter increments the total number of points counted for that particular phase. After counting at least 2000 points (for a fine-grained sample), the modal composition of the sample is determined.

7. The reflected light microscope

A variety of properties can be studied in reflected light, but these are generally qualitative in character, and rarely provide an unequivocal identification of a mineral phase.

Qualitative optical properties are made with either the polarizer inserted (and the analyzer out) or with both polarizer and analyzer inserted. Observations are made in air or with oil immersion objectives. Colour, reflectance, birefringence, and reflection pleochroism are observed in plane polarized light; anisotropism and internal reflections are observed under crossed polars.

8. Reflectance

The amount of light incident on a polished surface of a particular mineral depends on its reflectance. Both colour and degree of polishing can produce an anomalous amount of reflection. Although the eye cannot measure reflectance directly, it is possible to arrange minerals in order of reflectance.

9. Bireflectance and Reflection Pleochroism

Cubic minerals remain unchanged in reflectance and colour on rotation of the stage whatever the orientation of the grains. Basal sections of hexagonal and tetragonal crystals will also appear the same as cubic minerals.

10. Anisotropism

When the polished surface of a cubic mineral is examined under crossed polars, it is found to remain in extinction in all positions of the stage, whatever the crystallographic orientation - it is said to be isotrophic. Variation in the colour of anisotropic minerals, when the stage is rotated, can cautiously be used as an aid in identification.

11. Internal reflections

Some minerals examined in polished section are transparent and others opaque. Internal reflections are observable in the more transparent of the opaque minerals.

12. Hardness

Polishing and scratch hardness are useful tools in the identification of opaque minerals. To observe the polishing hardness, the KALB light line is used (Shelley, 1975). To observe this line, focus on the boundary line between two mineral grains, lower the stage so that the sample begins to go out of focus, and observe a 'line' of light which will move towards the softer mineral provided there is significant relief.

13. Structural and morphological properties

Crystal form and habit are recognizable in reflected light. Some minerals form well-developed crystals (euhedra), whereas others are anhedral. All of the standard terms used for transmitted light can also be used.

Cleavage and parting are sometimes seen in polished surfaces as rows of triangular pits.

Twinning of crystals is often observed in reflected light.

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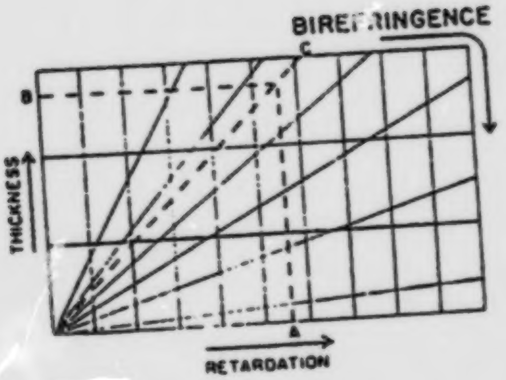
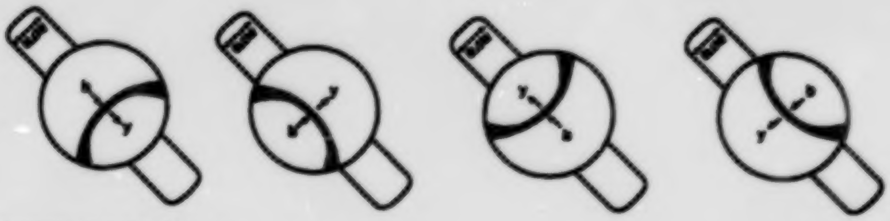
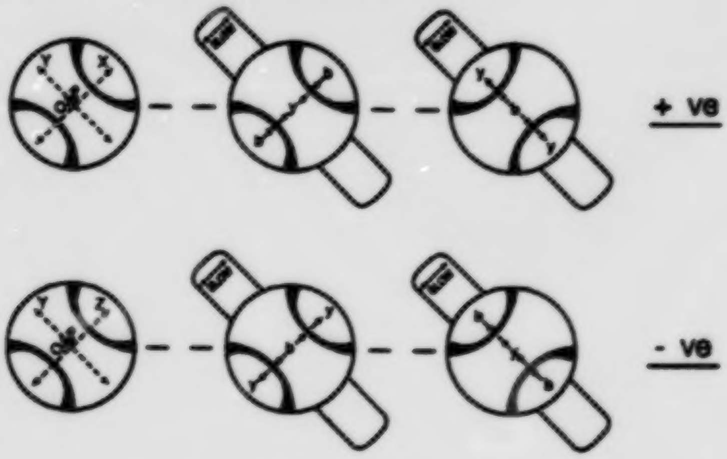

BIREFRINGENCE
C
B
THICKNESS
A
RETARDATION

Figure OM1. Diagram illustrating how the Michel-Levy chart is used.

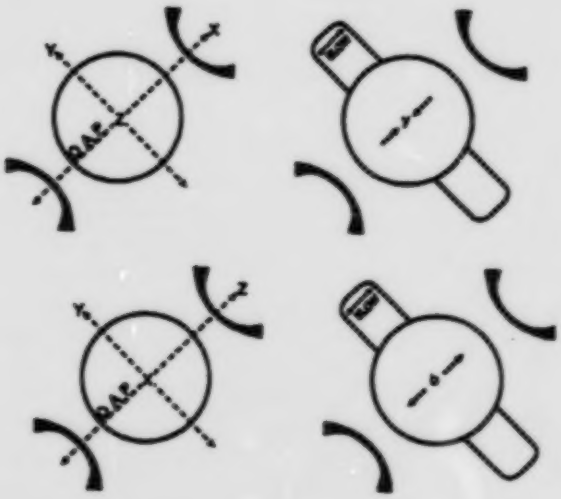


All +ve Schemes reversed for -ve.

Optic-axis figure of a biaxial +ve mineral using a sensitive tint plate or quartz wedge, b= blue, y = yellow, arrows indicate movement of colour rings when wedge inserted.



Distinction of biaxial +ve from biaxial -ve acute bisectrix interference figures using a sensitive-tint plate or quartz wedge, b = blue, y = yellow; arrows indicate movement of colour rings when wedge inserted.



Distinction of biaxial +ve from biaxial -ve acute bisectrix interference figures using a sensitive-tint plate or quartz wedge, b = blue, y = yellow; arrows indicate movement of colour rings when wedge inserted.

Figure OM2.

X-RAY POWDER DIFFRACTION

Introduction:

X-ray powder diffractometry (XRD) is a widely used diffraction technique for the precise and rapid identification of crystalline materials. However, complications occur when mineral mixtures are used and it is preferable to use monomineralic powder mounts when an unequivocal result is desired.

The following paragraphs summarise the principles of the technique. In the X-ray diffractometer, a collimated beam of Cu X-rays (other radiations such as Mo, Cr, Fe, & Co, can be used but Cu X-rays are the most commonly used) falls on a finely ground sample in which the crystallites have a random orientation. Diffraction of the X-rays occurs from planes of atoms making up the crystalline lattice. The direction in which the diffracted beam travels is dependant on the spacing between successive parallel planes of atoms in the lattice and this is given by the Bragg equation:

$$\lambda = 2d \sin\theta$$

where, d = the interplanar spacing
λ = wavelength of the X-ray, e.g. 1.542Å for Cu K
θ = angle of incident radiation to the plane of atoms

Different planes within the crystal will each give a reflection (hkl reflection) at a particular angle, thus defining a unique diffraction pattern characteristic of that particular crystal somewhat analogous to a fingerprint. In a randomly oriented sample all planes giving reflections will be suitably oriented to give a reflection. Some minerals tend to have a preferred orientation because of their habit or tendency to break along certain cleavage directions. These minerals, the most notable of which being the clay minerals and micas, will only give a few of the total refections possible. Recognition of these minerals can be difficult but usually they have one intense line (normally the 001) that can be used to identify them; the difficulties arise when two minerals having 001 lines close together are present in the same sample. This is often the case in mixtures of clay minerals, for which XRD is the most reliable method of identification; therefore, a variety of special techniques have been developed to reliably identify clays.

Instrumentation. The X-ray diffractometer consists of a source of radiation, a diffractometer, and a detection and counting system. The most common type of source is an X-ray sealed tube system which consists of a heated tungsten filament firing electrons at a copper anode (for Cu X-rays) from which X-rays are emitted. The electrons are accelerated towards the anode by means of a high potential which is supplied by the high voltage generator. Large amounts of heat are generated by this process and water cooling is essential. The intensity of the X-rays is directly dependant on the current and voltage used, which must never exceed the rating for that tube. Tube life will be prolonged by use of a voltage and current below the maximum.

The diffractometer has a specimen holder which rotates at an angle (θ) relative to the parallel beam. The detection system is on an arm rotating at an angle of 2θ. Both the incident and diffracted beams are collimated by a series of parallel slits. The divergence of the beam is further limited by a divergence slit which is normally 1°; a narrower slit of 1/4° is used if low 2θ angles are to be used. The size of the receiving slit on the detector arm governs the width of the line profile; narrow slits will therefore allow better resolution. The use of narrow divergence or receiving slits reduces peak intensities and minor peaks will be lost in the background. The detector normally used is a proportional counter. The diffracted beam is also passed through a crystal monochromator which allows only Cu Kα radiation to pass thus ensuring a monochromatic beam.

Safety advisory:

1. As X-rays are involved, film badges must be worn and the working area is restricted to authorized personnel only. Although the instrument has been constructed in a manner to ensure there is no X-ray leakage, a geiger counter should be regularly used to check for this possiblity. Note that the shutter should be closed when the operator is changing the removable slits to avoid leakage of X-rays from the slot.

Method:

X-ray powder diffractometry involves the following steps:

1. Sample preparation - the sample is ground to a fine powder in alcohol and the slurry is smeared onto a glass slide. To ensure randomly oriented mounts, a back-packing technique should be used. Preparation of clay mineral samples is given in the following section.

2. The sample is scanned in the diffractometer generally from 5° to 70° 2θ.

3. The peaks are located on the chart and the d-spacing calculated.

4. The pattern is indexed and the constituent phases are identified.

5. Special treatments for clay minerals and metamict (see below) minerals may be used.

Apparatus:

- Agate mortar and pestle
- Petrographic glass slides or sample mounts
- Drying lamp
- Furnace (to 1200°C)
- Desiccators
- Ultrasonic bath
- 60°C oven

Reagents:

- Alcohol
- Ethylene glycol
- Hydrochloric acid, HCl, 20%
- Hydrogen peroxide, H_2O_2
- Sodium hexametaphosphate

Procedures:

1.1. Using a mortar and pestle, crush a small piece (<0.5g) of the rock or if possible the individual minerals to a fine powder, in alcohol, (which helps prevent loss of material due to fragments flying off). The optimal size is about 10 microns and the powder should not feel gritty in the mortar.

1.2. Spread the slurry evenly over two-thirds of the glass slide and let it dry, under a heat lamp if necessary. Ideally, the sample should be one layer thick. If only a small amount of sample is available a low background holder such as a specially cut quartz crystal or an iron plate should be used.

1.3. Some samples are received already crushed for chemical analysis. If sufficient powder is available fill one of the special aluminum well mounts. A glass slide is held against the front and the powder is poured in through the opening at the side. tapping the mount so that the powder is packed down. This method is useful when one wants to avoid preferred orientation. Check that the powder is sufficiently fine before packing it; further grinding in the mortar and pestle is usually necessary.

1.4. The powder mount is placed in the diffractometer using the spring clip to hold it. The sample should be right up against the aluminum block above the spring clip for it to be evenly illuminated by the X-ray beam.

1.5. **IMPORTANT!** - turn the water cooler on.

1.6. The diffractometer will have been set up by the Philips service engineer. The settings for the detector and measuring circuits are standard and are given in the manual. They do not need to be changed in ordinary operation.

1.7. Turn the mains power on. The diffractometer arm should zero itself; if not, turn it off and on again until it does so.

1.8. Turn on the power to the X-ray tube. The voltage and current dials should be at zero or else the safety device will not allow the tube to turned on. Increase the voltage gradually to 40 kV and then the current to 20 mA. These are the standard settings and cover most types of analysis.

1.9. Check that the divergence and receiving slits are the 1° slits.

1.10. Set the 2θ ranges on the dials: the usual range is 5° to 70° 2θ. Set the minimum position at the lower angle and advance the diffractometer arm to it before opening the shutter or else the beam will shine directly into the detector and may damage it.

1.11. Turn the chart recorder on and advance the paper until the pen is at a major division. The chart drive is set at 2 cm per minute in normal operation. Open the shutter and press the automatic start button to begin the scan. The scan rate is set at 2° 2θ per minute.

1.12. When the scan is over close the shutter and change the sample. The next scan can be started as above.

1.13. Peaks on the previous chart can now be identified and their 2θ angle marked. A rule of thumb for distinguishing peaks is that they be at least two times background. The d-spacing can then be read of a chart which gives the d-spacing for a given 2θ angle for Cu radiation. The peaks are then ordered in terms of intensity; for most purposes only the three or four most intense peaks need be ordered but the process for mixtures is more complicated. The indexing of the pattern can now take place.

2. Indexing

The Hanawalt system is used for the indexing of patterns. This system takes the three strongest intensities on the pattern and uses the JCPDS search manual which lists the intensities for almost 48,000 patterns. This is a huge volume of information which would make searches long and difficult as well as giving many different possibilities for each pattern. Fortunately, there are a number of ways of dealing with this information overload. As this laboratory deals almost exclusively with minerals we need only to use the JCPDS Mineral sub-file which lists every known naturally occurring substance - some 3,500 in all. Secondly, some preliminary information about the unknown mineral is usually available; this would include knowledge of the mineral properties (colour, hardness, etc), crystallography and mineral association. All of this information is helpful in matching the pattern. The most useful data would be the chemistry of the mineral as the minerals are listed chemically.

Indexing a pattern using the Hanawalt system, the following steps may be used:

2.1. Identify the three strongest lines.

2.2. Turn to the section in the search manual covering the strongest line.

2.3. Taking the second strongest line, scan the second column in the section and match it.

2.4. Looking at the first and third lines in this area attempt to match the unknown, using the five other lines for confirmation and any additional information that is known about the sample. The d-spacings may not agree exactly because of instrumental problems or solid solution but the overall pattern should be the same. Note too, that variations in the intensity of some lines may occur because of a coarse sample or preferred orientation.

2.5. For a proper match the JCPDS card should be examined and all the peaks indexed with reference to the card.

For mixtures of several minerals the procedure is much more complex as the ordering of intensities is difficult. In most rock samples, however, there are recognizable minerals and their peaks e.g. quartz at 26.6° 2θ. The full pattern of each mineral is subtracted and the search is then done on the residual pattern. Identification of trace phases in such mixtures can be almost impossible particularly if these minerals are strong absorbers of the particular radiation used e.g., iron minerals with Cu radiation.

Special problems may occur with mineral solid solutions where the mineral composition lies between two end-members e.g. olivine where the composition may lie between Mg and Fe end members. The diffraction lines will shift accordingly between the two extremes and allowances will have to be made for this shift when the search is being conducted.

3. Identification of metamict minerals

Certain minerals which contain radioactive elements may not give a pattern or one that is impossible to match. This is because the radioactive disintegrations have disrupted the crystal lattice forming what are termed metamict minerals. In most cases the original pattern may be recovered simply by heating the sample at 1000°C for one hour and re-running it. One possible complication is minerals that oxidize e.g. UO_2 to U_3O_8.

Quality Control:

The above technique is a qualitative means of identification, although abundances can be estimated using the relative intensities of each phase present. The absorption effect is variable for each mineral present, so these relative intensities can be misleading - particularily if iron minerals are present.

A quartz sample should be run regularly to check that the pattern obtained is the same as the standard JCPDS one. If not there may be an alignment problem. The detection limits of minor phases depends entirely on their chemistry and on whether the mineral is likely to have a preferred orientation which may enhance one of its lines. A detection limit of 1% is assumed by most workers (Klug and Alexander, 1971)

Productivity:

Eight to ten samples can be run and indexed in a day.

Bibliography:

Jenkins, R. & de Vries, J.L., 1972, An introduction to X-ray powder diffractometry, Philips, 41 pages.

Klug, H.P. & Alexander, L.E., X-ray diffraction procedures for polycrystalline and amorphous materials. Wiley, New York, 1974, 716 pages.

Starkey, H.C., Blackmon, P.D., & Hauff P.L., 1984, The routine mineralogical analysis of clay-bearing samples, USGS Bulletin, 1563.

X-RAY DIFFRACTION IDENTIFICATION

Introduction:

Clay minerals by definition occur as particle less than 2µ in size. Their identification poses special problems because of their small particle size. Over the last four decades clay mineralogists have developed a variety of techniques for clay mineral identification of which XRD has been the most important by far. A large number of pre-treatments have become available for positively identifying clays but only two of these are routinely used: glycolation and heating. The preparation of clay samples is also different as the clay size fraction has to be separated out. In the Geoscience Laboratories the preparation forms part of the grain size analysis procedure which is usually requested at the same time (Refer to page MS4-1).

Method:

The method consists of the following techniques:

1. Clay preparation.
2. Clay separation.
3. Clay tile preparation.
4. X-ray diffraction.

Procedures:

1. Clay preparation for X-ray diffractometry

Clay preparation is performed from the -230 mesh (-63 micron) fraction. The three pretreatments given below are only used where excessive organic or carbonate content will interfere with the analysis. Dispersal of the clay minerals should be carried ultrasonically and the use of a deflocculant such as sodium hexametaphosphate should be a last resort.

1.1. Add H_2O_2 to remove organic (colloidal) matter.

1.1.1. Add 5 ml amounts of 30% H_2O_2 to a soil-water mixture of 1:1 (ca. 25 g of soil); heat lightly and stir occasionally.

1.1.2. Add H_2O_2 until the reaction stops or use light heat (ca. 80°C for several hours) to complete the reaction.

1.2. HCl; NaOAc buffer, or CH_3COOH removal for carbonates.

1.2.1. If there is a large amount of carbonate material, add 50 ml of 5N NaOAc.

1.2.2. If there is a small amount of carbonate, add 25 ml 1N HCl and dilute solution to 250 ml.

1.2.3. Repeat treatments as necessary.

1.2.4. The pH of the solution should be no more acidic than 3, for prolonged periods.

1.2.5. This procedure should leave a clear solution within an hour or two, with a slurry at the bottom; decant this solution.

1.3. Treat with sodium hexametaphosphate to disperse the suspension.

1.3.1. To the 25 ml soil-water suspension, add 25 ml of 50 g/l stock solution of sodium hexametaphosphate.

1.4. Wet-sieve through 230 mesh.

2. Clay separation

2.1. Start with 1000 ml suspension of dispersed solution

2.2. Shake cylinder vigorously for one minute with a stopper over the top.

2.3. Let suspension stand for either 6 hours and 3 minutes or 3 hours and 2 minutes and draw off circa. 75-100 ml of suspension from depths of 8 cm or 4 cm respectively, using a rubber bulb pipette.

3. Clay tile preparation

3.1. Let the 100 ml suspension settle for a day or so in a covered jar.

3.2. When ready to prepare the tiles, carefully decant 90 ml of the clear liquid and stir the remainder to a slurry.

3.3. Fill an eye-dropper with the slurry and spread it evenly over two glass slides and a porous ceramic tile.

3.4. Allow to dry. The timing of this preparation should be such that the samples are just dry when the XRD scan is made. Late afternoon is preferable as the tiles can air-dry overnight on the bench.

3.5. The preparation above will give a sample that has a preferred orientation and with an intense 001 line which is desirable. If the full pattern is required a randomly oriented mount will have to be prepared by drying the sample and back-packing the sample in an aluminum holder.

4. X-ray diffraction

4.1. Run one of the glass slides from 2° to 38° 2θ using a 1/4° divergence slit.

4.2. Place the other glass slide in a desiccator with a bowl of ethylene glycol in the bottom and leave in an oven at 60°C for at least 4 hours. The sample must be run immediately on removal from the desiccator.

4.3. The sample on the porcelain tile should be heated to 400°C for at least a half-hour and then run on the XRD.

4.4. This sample is then reheated to 550°C for at least a half-hour and re-run. The heated samples should be run immediately on removal from the furnace.

4.5. Interpretation of the patterns may carried out using the indexing procedure described above or a flow sheet for clay mineral identification as in Starkey et al. (1984).

Quality Control:

The above technique is a qualitative means of identification, although abundances can be estimated using the relative intensities of each phase present. The absorption effect is variable for each mineral present, so these relative intensities can be misleading - particularily if iron minerals are present.

A quartz sample should be run regularly to check that the pattern obtained is the same as the standard JCPDS one. If not there may be an alignment problem. The detection limits of minor phases depends entirely on their chemistry and on whether the mineral is likely to have a preferred orientation which may enhance one of its lines. A detection limit of 1% is assumed by most workers (Klug and Alexander, 1971).

Productivity:

Eight to ten samples can be run and indexed in a day.

Bibliography:

Jenkins, R. & de Vries, J.L., 1972, An introduction to X-ray powder diffractometry, Philips, 41 pages.

Klug, H.P., & Alexander, L.E., X-ray diffraction procedures for polycrystalline and amorphous materials. Wiley, New York, 1974, 716 pages.

Starkey, H.C., Blackmon, P.D., & Hauff P.L., 1984, The routine mineralogical analysis of clay-bearing samples, USGS Bulletin, 1563.

DETERMINATION OF SPECIFIC GRAVITY

Introduction:

Specific gravity is determined on a routine basis for job samples that have been submitted for whole-rock geochemical analysis. Specific gravity can also be determined for other rocks and minerals where the geologist or prospector has clearly identified this test.

Specific gravity is often used to confirm whether a rock is felsic, intermediate or mafic. Mafic rocks will have a higher specific gravity because of the presence of iron and magnesium bearing minerals.

Safety advisory:

1. There is no specific safety advisory for this method.

Method:

1. Weighing of the dry sample, followed by weighing of the sample when wetted.
2. Calculation based on the difference of the two weights.

Apparatus:

- Top-loading balance
- Bucket of water large enough to handle most samples, with suspended mesh basket

Reagents:

No specific reagents are required for this method.

Procedures:

1. Weighing of samples

1.1. Weigh dry sample on top-loading balance to at least one decimal place.

1.2. Place the sample in the water bucket so that it is covered; remove and suspend on mesh basket beneath the balance and record the weight of the sample suspended in water to at least one decimal place.

2. Calculation of results

$$S.G. = \frac{DW}{DS - SW}$$

where, S.G. = specific gravity
DW = dry weight, and
SW = suspended weight

Quality Control:

The Geoscience Laboratories has a rock 'standard' which should be checked at the beginning and end of each job.

Productivity:

A technician should be able to complete 100 determination per day.

Additional notes:

1. The balance should be calibrated often.
2. Note any sample peculiarities, e.g., vesicles.
3. Do not use this method on fragile samples such as clays.

DETERMINATION OF THE MOISTURE CONTENT OF SOIL (ASTM D2216-71)

Introduction:

Moisture (or water content) of soil is the ratio expressed as a percentage, of the weight of water in a given mass of soil to the weight of the solid particles.

Procedure:

1.1. Record the weight of a clean, dry container and lid (W1). A tight-fitting lid is essential.

1.2. Place a crumbled sample loosely in the container and replace the lid. Weigh the container, lid, and contents (W2).

1.3. Remove the lid and place container, lid, and contents in an oven at 105°C until a constant weight is reached (generally overnight).

1.4. After drying, remove container, lid, and contents from oven, replace the lid, and allow to cool.

1.5. Weigh the container, lid and contents (W3).

Calculation :

$$\%\ moisture\ in\ sample = \frac{W2 - W3}{W3 - W1} x\ 100\ \%$$

FIRE ASSAY

Introduction:

Fire assaying is used to determine the precious metal content of rocks and ores. Determinations of gold and silver present in abundances exceeding 0.01 oz/ton for Au and 0.10 oz/ton for Ag are made by fire assay and gravimetric techniques. Gold, platinium and palladium present in lower abundances are determined by Atomic Absorption Spectroscopy (see Section EA21) following fire assay preconcentration.

Special caution is required when dealing with unusual rock matrices, and it is critical that the flux composition be modified according to the composition of the sample. If an estimate of the gold or silver content is available, then the weight of the sample used can be adjusted.

Precious metals are normally present in nature at concentrations of less than 1 ppm. Furthermore, their distribution within a sample may be very inhomogeneous. The fire assay procedure enables a large sample to be analyzed in order to optimize precision and accuracy.

Safety advisory:

A lead flux is used to prepare the button. Lead is a known carcinogen, and has been linked to various chronic forms of cancer. The working area is a lead control area. Specific attention should be paid to the following points:

1. Ensure that fluxes are mixed ONLY in the vented hood.
2. Do not eat, drink or smoke in the room.
3. Wash your hands after handling flux.
4. Wear a fire-resistant lab coat in the fire assay area. Keep this coat in the area and do not remove it from the assay suite except to be laundered.
5. Wear a full face shield and insulated gloves when using the furnace.
6. Perform all parting processes in a fume hood.
7. Wear safety glasses when not wearing the full face shield.
8. Read MSDS sheets for all chemicals used in this method, i.e. litharge, sodium carbonate, silica, and borax glass.

Method:

There are three fire assay methods:

1. A regular gold and silver fire assay utilizing gravimetry.
2. A fire assay/graphite furnace technique for Au, Pt, and Pd.
3. A fire assay/nickel sulphide concentration technique, with analysis by instrumental neutron activation analysis.

Method #1 consists of the following techniques:

1. Sample preparation - the weighing and mixing of the rock powder and flux
2. Preconcentration - the melting and pouring to form a button, removing and cubing of the button, and cupelling to produce a prill
3. Determination - weighing and parting
4. Calculation of the results - weighing of the gold and converting this weight to oz/ton

If concentrations of less than 0.01 oz./ton Au, Pt, or Pd, or 0.10 oz/ton Ag are to be determined; the prill is passed to the Chemistry subsection for dissolution and analysis by graphite furnace AA (Method 2). The nickel sulphide fire assay (Method 3) is detailed later in this section.

Apparatus:

- Two regular fire assay furnaces used to prepare beads. One is used for ore-grade material, and the other for low abundance samples
- One cupellation furnace for the preparation of the prill
- Pouring plates, crucibles, cupels
- Balances capable of weighing to 0.01 mg
- Parting dishes and acid dispenser
- Fume hood

Reagents:

- The stock flux contains the following:

TABLE FA1.

Component	Weight (g)	%
litharge	66	55
sodium carbonate	33.6	28
silica	9	7.5
borax glass	8.4	7
flour	3	2.5

Nickel sulphide buttons require the use of:

- nickel carbonyl
- sulphur
- silica gel
- sodium carbonate
- sodium metaborate

Method 1: Conventional Fire Assay Method

Procedures:

1.1. Weigh out rock pulp (14.583 g, 1/2 assay ton) into a 20 g crucible.

1.2. Add pre-mixed stock flux (approximately 120 g).

1.3. Mix rock pulp and flux in crucible.

1.4. The position of each sample in the furnace is noted (it is not possible to write on the crucible unless a GRAPHITE pencil is used).

1.5. Place in assay furnace (preheated to 1025°C) and heat for 35 minutes.

1.6. Pour molten charge into cast iron mold.

1.7. Inspect crucible for lead loss (Figure FA1).

1.8. Note slag colour for possible interferences.

1.9. Note size and appearance of lead button.

1.10. Break slag and free the 20-25 g lead button.

1.11. Hammer the lead button into a cube.

1.12. Place the lead cube on a preheated cupel (950°C) and heat in the furnace for approximately half an hour, until lead is absorbed in cupel.

1.13. Remove the silver prill and note any peculiarities.

1.14. Brush and accurately weigh the silver prill using a fine balance (to 0.1 mg). Place the prill in a parting dish.

1.15. Digest silver prill in hot nitric acid and wash the residue with distilled water (fume hood operation).

1.16. Anneal and then accurately weigh the gold using a fine balance (to 0.01 mg).

1.17. Record all observations and results in a daily log.

1.18. Calculate silver weight and record gold and silver results in report. Assuming 1/2 assay ton, multiply the weight Ag (in g) by a factor of 2 and convert to oz/ton by division by 29.166.

Quality Control:

The determination limits for this method are 0.01 oz/ton for Au and 0.10 oz/ton for Ag.

The precision (2) at 10 times determination limit for Au is ±0.01 oz/ton, and ±0.10 oz/ton for Ag

Precision and accuracy are monitored by measuring the concentrations of gold and silver in at least one duplicate sample from each batch, and by analyzing the MRB gold/silver standards (MRB25-28) on a monthly basis. Proposed in-house certification data for these standards are:

TABLE FA2.

Standard	Gold		Silver	
	oz/ton	ppm	oz/ton	ppm
MRB25	1.44	49	2.2	75
MRB26	0.37	13	10.1	346
MRB27	0.016	0.5	45.1	1546
MRB28	1.45	50	94.5	3240

Productivity:

A technician should be able to complete up to 100 samples per day.

Additional Notes:

1. Bead colour - the presence of high concentrations of the platinum group elements may give the silver bead a dark grey colour.
2. Bead shape - flat silver beads usually contain some base metals, i.e. zinc.
3. Special assays (assays of complex or unusual ores): changes to the stock flux or standard assay method are often necessary with complex or unusual ores.
4. In the standard assay, the dilution of the pulp is approximately 1:5. However, an unusual chemistry of the pulp can still result in anomalous results. For example, excess silica may cause precious metals to be lost by slagging or matte formation. A knowledge of the pulp, fluxes, and reagents available will allow for the adjustment of the assay process to give accurate and reproducible results.
5. Other assays (bullion, umpire, and fraud case assays): these categories of assay, although identical to the regular gold and silver assays or special assays, require replicate analysis.
6. The various reagents (fluxes, reducing, oxidizing, and desulphurizing agents) and processes used during regular fire assay work are:

   A) Acid fluxes such as silica (SiO_2) and borax glass ($Na_2B_4O_7$) for use with basic ores

   B) Basic fluxes such as sodium carbonate ($NaCO_3$) and litharge (PbO) for use with silicic ores.

   C) Oxidizing agents such as potassium nitrate (KNO_3) used with strongly reducing ores such as sulphides, by roasting at 650°C.

   D) Reducing agents such as carbon-flour and Argol used with strongly oxidizing ores.

   E) Desulphurizing agents such as Na_2CO_3, PbO, and KNO_3 help to remove excess sulfur from the charge.

Method 2: Fire Assay Preconcentration with Determination of Au, Pt, Pd by GFAAS

Procedure:

2.1. Weigh 10 g of rock pulp.

2.2. Mix the pulp with 120 g of the standard flux (refer to conventional fire assay method, page MS14-2).

2.3. Add one drop of silver nitrate ($AgNO_3$) solution to make a bead of about 15 mg.

2.4. Mix the pulp and reagents in a crucible.

2.5. Place the crucible in preheated furnace at 1025°C and heat for 35 minutes.

2.6. The position of each sample in the furnace is noted (it is not possible to write on the crucible unless a GRAPHITE pencil is used).

2.7. Pour and inspect the crucible for lead loss.

2.8. Note the slag colour for possible interferences.

2.9. Note the size and appearance of the lead button.

2.10. Break the slag and free the lead button (20-25 g).

2.11. Cube the button with a hammer.

2.12. Place the lead cube on a preheated cupel (950°C) and heat in the furnace for approximately 30 minutes, until the lead is absorbed by the cupel, in the vented atmosphere.

2.13. Remove the silver prill and note any peculiarities.

2.14. Pass the bead on to the Chemistry subsection for graphite furnace AA analysis.

Quality Control:

The determination limit for Au is 2 ppb, and 1 ppb for Pt and Pd.

The precision (2σ) at 20 ppb is ±10 ppb for Au, and 5 ppb for Pt and Pd.

Blanks and the MRB-27 standard reference material are processed with every batch of samples for quality control purposes.

Additional Notes:

1. For samples with low concentrations (<0.01 oz/ton Au, Pt or Pd and <0.10 oz/ton Ag) of precious metals, it is preferable to use the dedicated low blank furnace.
2. Other assays (bullion, umpire, and fraud case assays): these categories of assay, although identical to the regular gold and silver assays or special assays, require replicate analysis.

Method 3: Nickel sulphide fire assay

Procedure:

The noble metals are inhomogeneously distributed in rocks and ores, forming discrete noble metal minerals and possibly occurring in solid solution in rock-forming minerals, chromites, and sulphides. The nickel sulphide fire-assay technique quantitatively collects all the platinum group metals (PGE) and gold from a large sized sample. The bead is dissolved in 12 N HCl; the residue is collected on filter paper and irradiated.

The noble metals on the filter paper can be determined by instrumental neutron activation analysis. Full details of apparatus, reagents, and sample preparation are given in Hoffman et al. (1978).

3.1. Preparation of charge

3.1.1. Samples are ground following standard procedures (pages MS1-2 to MS1-5), and submitted for geochemical analysis for the elements Ni, Cu, Co, Cr, and S. Nickel and sulphur values are critical in the determination of the charge composition. Elevated copper values may indicate low concentrations of some of the PGE. High chrome samples may indicate the presence of chromite which will interfere with the precious metal recovery.

3.1.2. Samples are prepared in duplicate such that a 24-34 g button is prepared which contains ca. 16 g Ni, 10 g S, and all noble elements. The charge composition is calculated in four stages:

STAGE 1:

If the pulp contains >20 Wt. % S, then the sample size is selected so that the button contains only 10 g sulphur, i.e. if the sample contains 30% S, then the amount of pulp used is 1000/30 = 33.3g.

If 1 Wt. % < S < 20 Wt. %, 50 g of pulp is used, and sufficient S is added so that the button will contain 10 g sulphur,

i.e.,

$$Wt.\ S\ added\,(g) \;=\; 10g - \left(\frac{S\ content\ of\ pulp(Wt.\ \%)}{2}\right)$$

If the S content is less than 1 Wt.%, only 40 g of sample is used, and 10 g of S is added.

STAGE 2:

The nickel content of the button should be ca. 16 g. To achieve this, the amount of Ni added is given by:

$$Wt.\ Ni\ added(g) =$$

$$16g - \frac{Wt.\ Ni\ in\ sample(g)\ x\ Wt.\ sample(g)}{100}$$

STAGE 3:

Silica is added to the charge:

If S<8 Wt. %, then no silica is added.

If 8 Wt. %<S<15 Wt. %, then 5 g of silica is added.

If 15 Wt. %<S<30 Wt. %, then 10 g of silica is added.

If 30 Wt. %<S<40 Wt. %, then 13 g of silica is added.

STAGE 4:

For each sample, 60 g of Na_2BO_4 and 30 g of Na_2CO_3 is added to the charge.

3.1.3. A standard reference material (SARM-7) together with one of the MRB PGE standards (MRB19-22) is included with each batch of samples. The SARM-7 standard may be prepared by mixing 9 g S with 15 g Ni, and adding 35 g of pulp. 60 g Na_2BO_4 and 30g $NaCO_3$ are also included, but no silica is added.

3.1.4. A 30 g assay crucible is used for the charge, and the components are thoroughly mixed. The position of the charge in the furnace is noted for each sample to avoid confusing the samples (it is not possible to write on the crucible unless a GRAPHITE pencil is used).

3.1.5. The charge is fused for 90 minutes at 1000°C in the Globar furnace. When the reaction is complete, the charge is removed from the furnace and cooled.

3.1.6. The nickel sulphide button is removed from the crucible with a hammer, and weighed.

3.1.7. The nickel sulphide bead is broken with the Rocklabs 'little smasher' (a hand held steel pulverizer), and the fragments are milled in zirconia or alumina mills to produce a fine powder of -70 mesh.

3.1.8. The sample is weighed to determine the loss during grinding, and samples are passed on to the Chemistry subsection for the concentration of the PGE, before determination by INAA.

3.2. Concentration of the PGE

The procedure for the concentration of the PGE from a crushed nickel sulphide button is outlined below:

3.2.1. The crushed button is heated with 400 ml of 12 N HCL in a covered beaker on a hot plate in a fume hood until the sample completely dissolves.

3.2.2. The solution is cooled and filtered under vacuum and washed with about 400 ml of distilled water. It is imperative that all the hydrochloric acid is removed; that includes any acid caught at the base of the vacuum filter apparatus. The compositional character of the filter paper is very important; Millipore (SWP 047-00) SM-type 5 micron 47 mm filter papers are best suited for this technique.

3.2.3. The filter papers are folded twice. The quadrant is then sealed inside special plastic using a bag-sealing unit. The bag is then itself sealed within another bag ready for the irradiation and counting procedure. **NOTE** that it is important that all bag seals are good and sturdy; this will avoid the escape of radioactive material from the bag during rough handling subsequent to the irradiation.

3.3. Determination by INAA

The PGE can be determined using a procedure involving two counts following Hoffman et al. (1978). Rhodium and palladium can be determined during the first count, and the remainder of the PGE during a second count.

Rhodium and palladium are determined by irradiation of samples serially for 5 minutes and then allowed to decay for 60 seconds so that the very short-lived radioisotopes can decay. Samples and standards were counted for 200 s for the 109mPd and 104mRh gamma-rays. Peak areas, corrected for background, are compared for samples and standards.

Palladium, platinum, osmium, ruthenium, iridium, and gold are determined up to 40 days after irradiation. Samples, ore standards, and elemental standards are sealed in plastic irradiation canisters and irradiated for 16 hours. Integrated peak areas, corrected for background, are used together with yields from crushing procedure, decay constant, irradiation time, counting time, and duration of count, to determine the concentrations in the unknowns.

Full details of the counting procedure are provided at the SLOWPOKE reactor facility.

3.4. Data Reduction

Two IBM-PC BASIC programs are used to reduce data; they prompt the user for information and input data. Copies of the programs are available from the Geoscience Laboratories.

Quality Control:

All samples and standards are analyzed in duplicate. SARM 7 and at least one of the MRB standards (MRB-19 through 23) are included with each batch of samples.

Bibliography:

Hoffman, E.L.,Naldrett, A.J.,Van Loon, J.C.,Hancock, R.G.V., and Manson, A., 1978, The Determination of all the Platinum Group Elements and Gold in Rocks and Ore by Neutron Activation Analysis after Preconcentration by a Nickel Sulphide Fire-Assay Technique on Large Samples, ANALYTICA CHIMICA ACTA, Vol. 102, pp 157-166.

TABLE FA3. DETERMINATION LIMITS .

Element	Determination Limit (ppb)	
Rh	1	(200 s count)
Pd	50	(200 s count)
Pt	5	(2500 s count)
Ir	0.1	(5000 s count)
Ru	3	(5000 s count)
Os	2	(5000 s count)
Au	0.1	(5000 s count)

Precision (2σ) values quoted by Hoffman et al (1978), based on multiple analysis of an internal standard (L.S. 4) are:

TABLE FA4. PRECISION (2σ).

Element	Concentration (ppb)	Precision (%)
Rh	135	5
Pd	320	12.5
Pt	290	10
Ir	75	6.7
Os	30	10
Ru	150	13
Au	42	14

Accuracy may be judged with reference to the expected values of SARM 7, and with reference to the results for the MRB-series standards. These values, expressed in ppb, are shown in Table FA5.

TABLE FA5.

Standard	Au (ppb)	Pt (ppb)	Pd (ppb)	Os (ppb)	Ir (ppb)	Ru (ppb)	Rh (ppb)
SARM 7	310	3740	1530	63	74	43	24
MRB-19	450	728	1784	10	37	65	228
MRB-20	269	1395	1154	24	48	108	149
MRB-21	5616	69872	243929	271	287	730	2362
MRB-22	1344	23551	71219	101	84	25	5876
MRB-23	2810	31643	90126	145	126	339	915

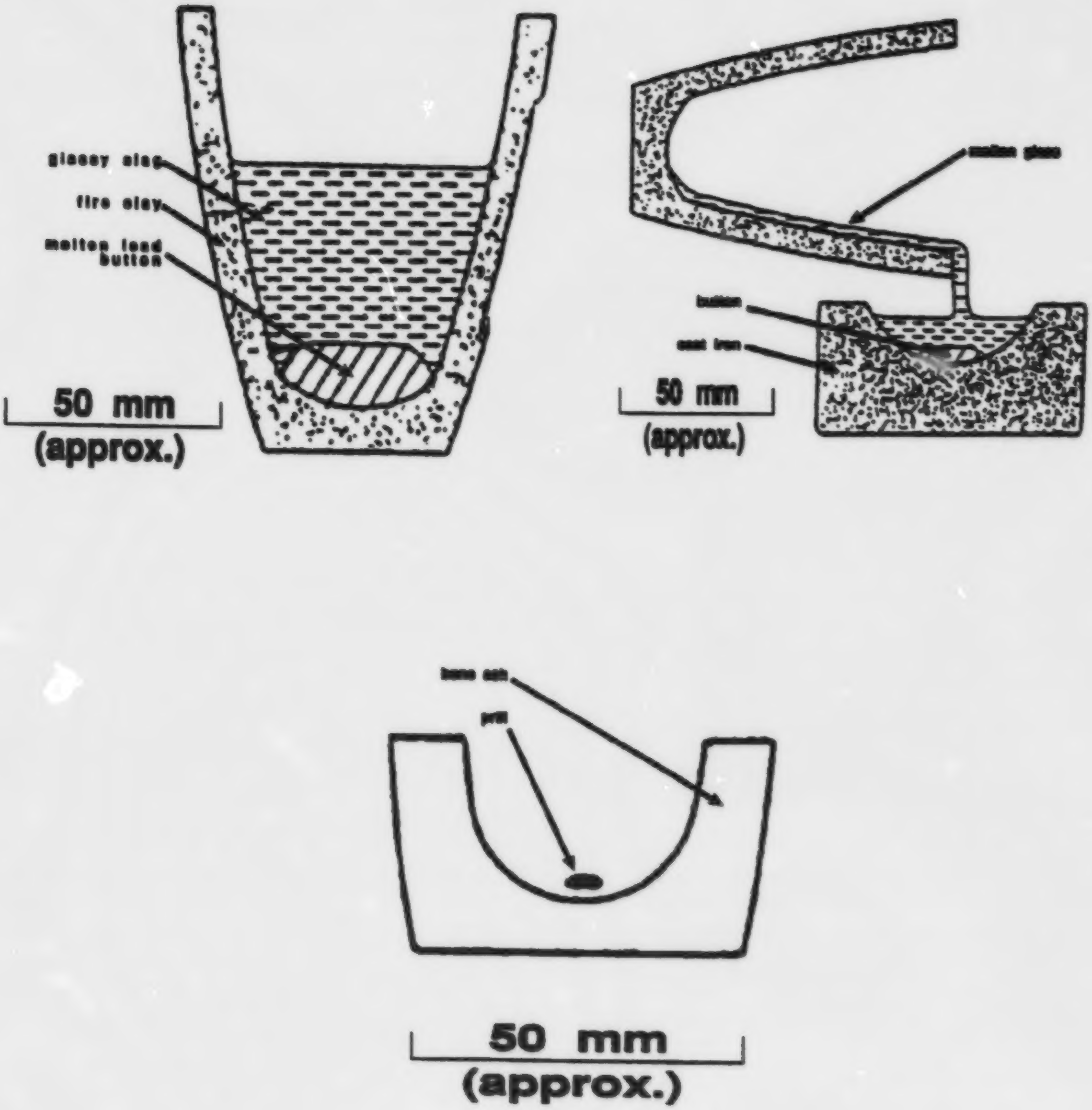

glassy slag
fire clay
molten lead button
50 mm (approx.)
molten glass
button
cast iron
50 mm (approx.)
bone ash
prill
50 mm (approx.)

Figure FA1.

NORMATIVE PROGRAMS

Introduction:

The CIPW system of rock classification was formulated about the turn of the century by Whitman Cross, Joseph Iddings, Louis Pirsson and Henry Washington.

The system recalculates the bulk chemical composition of a rock into a hypothetical assemblage of standard (normative) minerals. The calculation of the norms for different types of rocks, provides a method of classification by quantitatively studying and comparing the norms of unknown rocks.

The elements used in the calculations are usually expressed in the oxide form, and are given in Table NORM1. The CIPW norms (weight norms) are calculated by assigning amounts of the molecular properties to a standard set of mineral molecules as outline in Table NORM2. The molecular properties are the weight percent of the elemental analysis divided by the molecular weight.

The percentage of each mineral molecule is then calculated by multiplying the molecular amount of each constituent of each mineral by its molecular weight.

The Swiss mineralogist and petrographer, Paul Niggli, introduced an important change to the norm calculation by discarding the weight units and introducing the "equivalent molecular unit". These are based upon the number of cations in the mineral or oxide, e.g.

$$CaO.Al_2O_3.2SiO_2 = 5\ An$$
(formula has 5 cations)

1 An is equal to a quantity of anorthite containing one cation. Cation equations can thus be written easily, e.g.

$$4\ En = 3\ Fo + 1\ Q$$

$$2\,(MgO.SiO_2) = 2MgO.SiO_2 + SiO_2$$

In the norm calculations with Niggli's method, the molecular proportions are abandoned in favor of cation proportions. With this method all the elemental oxides constituents are reduced to one cation (See Table NORM3).

To calculate the cation proportions, the weight percent is divided by the equivalent molecular weight and multiplied by 1000. These figures are added and percentages of each cation iscalculated. The cation percentages are then assigned to the normative minerals according to the steps in the norm calculation.

TABLE NORM1.

Elemental Oxide	Approx. Molecular Weight	Elemental Oxide with Cation	Approx. Molecular Weight
SiO_2	60	SiO_2	60
Al_2O_3	102	$AlO_{1.5}$	51
Fe_2O_3	160	$FeO_{1.5}$	80
FeO	72	FeO	72
MgO	40	MgO	40
CaO	56	CaO	56
Na_2O	62	$NaO_{0.5}$	31
K_2O	92	$KO_{0.5}$	47
TiO_2	80	TiO_2	80
P_2O_5	142	$PO_{2.5}$	71
S	32	S	32
MnO	71	MnO	71

Normative Program Algorithm

Alteration of Raw Chemical Data

1. The Fe_2O_3/FeO ratio is adjusted according to the equation:

$$\%\ Fe_2O_3 = \%\ TiO_2 + 1.5$$

If Fe_2O_3 is less than this, no change is made; if it is greater, the excess is converted to FeO.

2. The total percentage is recalculated to 100 without the volitiles H_2O^+, H_2O^- and CO_2.

3. The cation % for MnO is added to that of FeO.

Algorithm

Once the chemical data have been adjusted, as indicated above, the program calculates the Norms based on the following steps:

1. Apatite is formed from P and 1.67 times this amount of Ca.

2. Pyrite is formed from S and half this amount of Fe.

TABLE NORM2. THE NORM MINERALS USED

Salic		Group
Quartz	Q	SiO_2
Corundum	C	Al_2O_3
Orthoclase	OR	$K_2O.Al_2O_3.6SiO_2$
Albite	AB	$Na_2O.Al_2O_3.6SiO2$
Anorthosite	AN	$CaO.Al_2O_3.SiO2$
Leucite	LC	$K_2O.Al_2O_3.4SiO_2$
Nepheline	NE	$Na_2O.Al_2O_3.2SiO_2$
Kaliophilite	KP	$K_2O.Al_2O_3.SiO_2$
Femic Group		
Wollastonite	WO	$CaO.SiO_2$
Enstatite	EN	$MgO.SiO_2$
Ferrosilite	FS	$FeO.SiO_2$
Acmite	AC	$Na_2O.Fe_2O_3.4SiO_2$
Magnetite	MT	$FeO.Fe_2O_3$
Hematite	HM	Fe_2O_3
Ilmenite	IL	$FeO.TiO2$
Apatite	AP	$3\,(CaO.P_2O_5).CaF_2$
Pyrite	PY	FeS_2
Hypersthene	HY	$(Mg,Fe)O.SiO_2$
Diopside	DI	$CaMgSi_2O_6$
Olivine	OL	$2\,(Mg,Fe)O.SiO_2$
Hedenbergite	HE	$CaFeSi_2O_6$

Table NORM3.

Elemental Oxide	Weight %	Equiv. Molecular Weight	Cation Proportions x 1000	Cation %
SiO_2	49.10	60	818	46.0
$AlO_{1.5}$	16.21	51	317	17.9
$FeO_{1.5}$	2.87	80	36	2.0
FeO	6.84	72	95	5.3
MgO	5.04	40	125	7.0
CaO	8.90	56	159	9.0
$NaO_{0.5}$	3.53	31	114	6.4
$KO_{0.5}$	2.76	47	59	3.3
TiO_2	3.59	80	45	2.5
$PO_{2.5}$	0.54	71	8	0.5
S	0.00	32	0	0
MnO	0.05	7	11	0.1

3. Ilmentite is formed from Ti and an equal amount of Fe.

4. If CO_2 is included in analysis, calcite is formed from CO_2 and an equal amount of Ca (if required CO_2 can be included in the program).

5. Orthoclase and albite are formed provisionally from K and Na respectively combined in the right proportions with Al and Si.

6. If there is an excess of Al over K and Na, it is combined with the right proportions of Ca and Si to form Anorthite.

7. If there is an excess of Al over the Ca it is calculated as Corundum.

8. If in (5) there is an excess of Na over Al it is to be combined with an equal amount of Fe^{3+} and twice as much Si to form Acmite.

9. The remaining Fe^{3+} is assigned to magnetite with half this amount of Fe^{2+}.

10. If there is still an excess of Fe^{3+}, it is calculated as Hematite.

11. Wollastonite is formed from the amount of Ca left and an equal amount of Si.

12. Enstatite and ferrosilite are formed provisionally from all the Mg and Fe^{2+}.

13. If there is an excess of Si, it is calculated as Quartz.

    If step (13) is true, the norm calculation is finished: otherwise, Si has been assigned beyond the original amount and is a negative quantity. The following steps bring Si back to 0 by the minerals of a lower degree of silification substituting in part or wholly for those minerals that were formed provisionally.

14. The amount of Mg and Fe^{2+} used to form Enstatite and Ferrosilite are added and the relative amounts of Mg and Fe^{2+} calculated using the ratios noted here.

$$\frac{Mg}{Mg + Fe^{2+}} \qquad \frac{Fe^{2+}}{Mg + Fe^{2+}}$$

15. If the amount of Ca in Wollastonite is greater than the total $Mg+Fe^{2+}$ all the Mg and Fe^{2+} will be converted with Ca to Diopside and Hedenbergite respectively. Diopside ($MgCa_2SiO_2$) is equal to 4 times the amount of Mg.

Hedenbergite ($FeCa_2SiO_3$) is equal to 4 times the amount of Fe^{2+}.

Wollastonite is now equal to its original value minus 2 ($Mg+Fe^{2+}$).

Enstatite and ferrosilite now equal 0.

16. If the amount of Ca in Wollastonite is less than the total $Mg+Fe^{2+}$ all of the Wollastonite will be converted to Diopside and Hedenbergite with the right proportions of Mg and Fe^{2+}.

$$\text{Diopside} = \frac{Ca(Mg)\, x\, 4}{Mg+Fe}$$

$$\text{Hedenbergite} = \frac{Ca(Fe^{2+})\, x\, 4}{Mg+Fe}$$

The remainder of $Mg+Fe^{2+}$ (= to the original minus Ca of Wollastonite) is calculated as Hypersthene.

There is no change in total Si in the above 3 steps because the minerals have been converted to other minerals with the same silicon content.

17. The necessary amounts of Hypersthene (if any) are converted to Olivine according to the equation:

$$4\,HY = 3\,Ol + 1\,Q$$

18. If these still is not enough Si in the analysis, Albite is turned into Nepheline according to the equation:

$$5\,AB = 3\,Ne + 2\,Q$$

19. If the analysis is very low in Si, Orthoclase is in part or wholly converted into Leucite.

$$5\,OR = 4\,LC + 1\,Q$$

20. In rare cases there is not even enough Si to form Leucite.

Then Kaliophilite is formed.

$$4\,LC = 3\,KP + 1\,Q$$

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ALKNORM FOR FELDSPATHOIDAL AND MELILITIC IGNEOUS ROCKS

Introduction:

Chayes and Yoder (1971) have underlined some of the inadequacies of the CIPW normative system when dealing with feldspathoidal and melilite bearing lavas. King (1965) experienced the same inadequacies for strongly alkaline undersaturated plutonic rocks. As a result, a calculation similar to that for the standard CIPW norm (Washington 1917; modified by Barth 1931) has been devised for these rarer igneous rocks.

The new calculations have been specifically created for ijolitic, nephelinitic, and melilite-bearing suites of igneous rocks but is also applicable to other undersaturated and strongly alkaline rocks which lack Ca-plagioclase. This would include the peralkaline syenites, alkali pyroxenites, peridotites, and nepheline syenites; ultra-alkaline rocks and volcanic equivalents of the classificatory system described by Nockolds (1954); and many of the feldspathoidal peralkaline and metaluminous rock types defined by Shand (1949).

The criterion governing the use of this norm is that it is appropriate for undersaturated rocks when either or both acmite or calcium ortho-silicate (CS) appear in the CIPW norm.

The main features of this norm are:

1. It allows the calculation of nepheline as $Na_3KAl_4Si_4O_{16}$, the formula preferred by Hamilton and Mackenzie (1960) and Barth (1963). In the CIPW norm, nepheline is calculated free of the kalsilite molecule ($KAlSiO_4$), which frequently gives rise to leucite in the norm and unnecessary silica deficiency elsewhere.

2. It favors the formation of the minerals pervoskite, sphene andradite, kalsilite, and melilite (both akermanite and gehlenite end members). A more actualistic melilite (i.e. showing the replacement of Ca by Na, and Al by Fe^{3+}) is not calculated because the geochemistry of melilite is not clear. The formation of the iron-bearing akermanite by desilicating diopside in IV, J of the calculation is governed by the relation:

   $4\ Ca(Mg,Fe)Si_2O_6 - 3SiO_2\ 2Ca_2(Mg,Fe)SiO_7 + (Mg,Fe)2SiO_4$

   Calcium orthosilicate is not calculated since it is quite unrealistic (Washington, 1915).

3. The significance of the roles of Ca and Fe, as well as the alkalis is demonstrated. In particular, instead of using all the ferric iron early in the calculation to form acmite and magnetite, as in the CIPW system, here some is retained till later to enable the possible formation of andradite.

4. It allows more realistic comparison with the mode and facilitates geochemical and mineralogical interpretation. However, amphibole and micas are not calculated, nor is ilmenite because it is not normally a common constituent in strongly alkaline and oxidized magmatic rocks:

Algorithm:

1. Determine the molecular proportions of the constituents in the chemical analysis by dividing the weight percentage of each by the molecular weight. Add MnO to FeO, and SrO and BaO to CaO.

2. If molecular $SiO_2 > FeO + MgO + CaO + 6(Na_2O + K_2O)$, then omit stages 3ei, 3eii, 3eiii; 4A; 4B; 4C; 4E; and 4K.

3. Allot molecular amounts in the order and in the ratios listed below.

   a. $P_2O_5 : CaO = 3:10$ for apatite

   b. $CO_2 : CaO = 1:1$ for calcite

   $CO_2 : MgO = 1:1$ for magnesite

   c. $SO_3 : Na_2O = 1:1$ for thernardite

   d. $F:Ca(O) = 2:1$ for fluorite

   ei. $K_2O : Al_2O_3 = 1:1$

   ii. $Al_2O_3 : Na_2O = 1:1$

   iii. combine i and ii to give $(K_2O.Al_2O_3):(Al_2O_3.Na_2O) = 1:3$ for nepheline

iv. residual $K_2O.Al_2O_3$ for kalsilite, leucite or orthoclase

v. residual $Na_2O.Al_2O_3$ for carnegieite or albite

f. residual $Na_2O:Fe_2O_3 = 1:1$ for acmite

g.residual $Al_2O_3:CaO = 1:2$ for gehlenite

h. residual Al_2O_3 for corundum

i. residual Na_2O for Na_2SiO_3

j. $TiO_2:CaO = 1:1$ for sphene or pervoskite (or rutile if no CaO)

k.If FeO remaining CaO, then allot excess $FeO:Fe_2O_3 = 1:1$ for magnetite; if not then continue to 12.

l. $(FeO + MgO) :CaO = 1:1$ for diopside (the ratio of MgO and still available FeO is calculated, and is maintained in 12/13, and any akermanite subsequently formed)

m. residual (FeO + MgO) for olivine

n. Fe_2O_3: residual $CaO = 1:3$ for andradite

o. residual Fe_2O_3 for hematite, or residual CaO for wollastonite

4. Allot silica to make the following normative minerals:

A. In 3, $3Na_2O.K_2O.4Al_2O_3.8SiO_2$ for nepheline

B. In 3, $K_2O.Al_2O_3.2SiO_2$ for kalsilite

C. In 3, $Na_2O.Al_2O_3.2SiO_2$ for carnegieite

D. In 3, $Na_2O.Fe_2O_3.4SiO_2$ for acmite

E. In 3, $2CaO.Al_2O_3.SiO_2$ for gehlenite

F. In 3, $Na_2O.SiO_2$ for Na_2SiO_3

G. In 3, $3CaO.Fe_2O_3.3SiO_2$ for andradite

H. In 3, $CaO.SiO_2$ for wollastonite (wol)

I. In 3, $2(MgO + FeO).SiO_2$ for olivine (fo and fa)

J. In 3, $CaO.(MgO + FeO).2SiO_2$ for diopside (wo, en and fs); if SiO_2 is insufficient, distribute between x molecules diopside, y molecules akermanite ($2CaO.(Mg,Fe)O.2SiO_2$), and y/2 molecules olivine, given by $2x + 2.5y =$ available SiO_2; and olivine formed to I. (N.B. Akermanite is recalculated in the norm as both the ordinary akermanite molecule $Ca_2MgSi_2O_7$, and the Fe-akermanite molecule, $Ca_2FeSi_2O_7$ in a manner similar to that for olivine.

K. If silica is insufficient for stages A-I; create the normative molecules in A-I and akermanite and olivine in J; and declare the silica deficiency (Si-def); if, however, silica remains, then continue allocation of SiO_2.

L. $ZrO_2.SiO_2$ for zircon; if no silica or insufficient, then remainder of ZrO_2 for baddeleyite.

M. In 10, $CaO.TiO_2.SiO_2$ for sphene, or as far as possible (remainder left as pervoskite $CaO.TiO_2$)

N. Convert B to $K_2O.Al_2O_3.4SiO_2$ for leucite or if possible $K_2O.Al_2O_3.6SiO_2$,or orthoclase (if the available SiO_2 is not sufficient for the conversions, then distribute between x molecules leucite and y molecules kalsilite, given by $x + y =$ available K_2O and $4x + 2y =$ available SiO_2, or between x molecules orthoclase and y molecules leucite, given by $x+y =$ available K_2O and $6x + 4y =$ available SiO_2, as appropriate)

O. Convert C to $Na_2O.Al_2O_3.6SiO_2$ for albite; if insufficient SiO_2, then distribute between x molecules albite and y molecules carnegieite, where $x + y =$ available Na2O, and $6x + 2y =$ available SiO2.

P. If silica remains, convert nepheline A to albite + orthoclase; if the available SiO_2 is not sufficient to convert all the nepheline, then distribute between x molecules albite + orthoclase, and y molecules nepheline, given by $x + 4y =$ available $Na_2O + K_2O$ in A, and $6x + 8y =$ available SiO_2 (but, maintain $Na_2O:K_2O = 3:1$ in nepheline); add any orthoclase formed to N and albite to O

Q. Any residual SiO_2 is calculated as quartz.

5. Determine the percentage weights of the normative minerals by multiplying the molecular propor-

tions of the minerals in 3 and 4 by the appropriate molecular weight.

Bibliography:

Le Bas, M.J., A Norm for Feldspathoidal and Melilitic Igneous Rocks, Journal of Geology, Vol 81, 1973, pp. 89-96.

PROTOCOLS FOR SAMPLE DIGESTION AND ANALYTICAL DETERMINATION IN THE ELEMENTAL ANALYSIS SUBSECTION

Introduction:

Samples received for analysis in the Geoscience Laboratories are classified: (1) under assigned job numbers or (2) as "assay" samples. Jobs comprise up to 50 samples and can require extensive analytical work including up to 70 elemental determinations for each sample. Priorities for these jobs are assigned by the Chief in consultation with the client geologist. "Assay" samples require a faster turnaround time and can require as little as one elemental determination; clients include the private sector and priorities for completion are set immediately and updated weekly.

Elemental analysis is divided into major element analysis, and trace element analysis. Each has a number of packages (M1, T1, etc.) which for convenience, group elements according to client requirements or analytical technique. A complete description of these analytical packages can be found in the Geoscience Laboratories "Analytical Capabilities and Services" booklet.

In addition to the elemental packages, an XRF Screen is implemented as an unreported monitor package to check for acid-resistant minerals with known acid digestion problems and unusual matrices.

Selection of Determination Technique

In general, the instrumental techniques used for each package are:

M1, M2, M3	XRF - alternate techniques include AAS and classical analysis involving gravimetric, volumetric and colorimetric techniques.
T1	AAS - including flame, graphite furnace and hydride generation techniques.
T2	ICP-OES
T3	XRF
T4, T5	ICP-MS
Screen	XRF

Selection of Samples to be Monitored with the Screen Program

1. All samples requesting the complete T2 and T4 package or any part of such packages require a Screen evaluation.

2. All samples requesting barium and chromium (AAS) or tin (ICP-MS) require a Screen evaluation.

3. All samples requesting major analysis which have a sulphur content 0.3% - 3.0%, should be checked for possible high arsenic using the Screen program. Although arsenic is not determined with the Screen program, its presence will be indicated as a high lead value.

Major Element Analysis

1. A carbon/sulphur determination is made on all samples for which any of the major element packages are requested.

2. If the sulphur content is <0.3%, proceed with fusion and determination by XRF.

3. If sulphur content is 0.3% - 3.0%, roast the sample prior to fusion. Request a Screen evaluation on the sample for arsenic content. Proceed with fusion and determination by XRF if the sample contains no appreciable arsenic.

4. If sulphur content is >3.0%, or high arsenic is suggested with the Screen evaluation, pass the sample to AAS for preparation and determination.

Major element analysis will be performed by AAS when

1. Less than 3 elements per sample are requested.

2. Sulphur content is >3.0% and/or arsenic content is suspected to be high. **DO NOT** attempt to fuse these samples in platinum crucibles. Damage to the crucible can occur with some sulphide bearing samples. A few hundred ppm As will scour a crucible; a few percent will destroy it.

3. Silica content is between 10 and 30 percent.

Programs for XRF determination in this range are not reliable.

4. Iron content is high (>50% as Fe_2O_3) and a glass bead for presentation to an XRF spectrometer is difficult to prepare.

Selection of Digestion Procedure

Acid attack:

1. Requests for T1 options and/or the T2 package, options or additions, require a HNO_3-$HClO_4$-HF attack. Any element determined by ICP-OES requires this acid attack.
2. Any "assay" sample requiring elements of the T1 options, which will be determined by Flame AAS only, may use a HCl-HF-HNO_3 acid attack.
3. Requests for silver and cadmium require an acid digestion without the presence of HCl.
4. Requests for a T4 or T5 package require a detailed HNO_3-$HClO_4$-HF attack.
5. Vegetation samples require dry ashing followed by mineral acid attack.

Fusions:

1. Samples requiring the determination of tin are fused with lithium metaborate by the sample preparation group and passed to ICP-MS for determination.
2. Sample residues, which indicate incomplete acid attack, are fused with an appropriate flux. The indication may be visual or after Screen evaluation.
3. For accurate work, use an acid attack followed by a fusion of any residue using a minimum of flux. The two solutions are combined and analyzed by the appropriate technique.

NOTE: Solutions presented to ICP-OES and ICP-MS must indicate the approximate total salt content.

4. Samples known to contain high barium (barite) and chromium (chromite) are fused with lithium metaborate without prior acid attack. If the chromium content is 5%, sodium peroxide is used as the flux. Only Flame AAS is used for measurement when the salt content of the solution is high.

Selection of Sample Weight/Volume

1. A 0.500 g sample, digested, and made to a final volume of 25 ml is the norm for requests for T1 and T2 elements. All subsequent dilutions are the responsibility of the personnel performing the final determination. Dilution factor 50.
2. Assay samples whose analytes are determined by flame AAS, use a 0.500 g portion of sample made to a final volume of 50 ml. Dilution factor 100.
3. The T4 package requires a 0.200 g of sample made to a final volume of 100 ml. Dilution factor 500.
4. Silver and cadmium digestion requires a 1.000 g sample made to a final volume of 25 ml. Dilution factor 25.
5. Less sample may be used and/or larger volumes chosen when elements normally considered as trace components are present at ore grade levels. These new dilution factors must be flagged for the attention of the instrument operator performing the final determination.

Quality Control:

1. Instrumental control and stability are monitored by the instrument operator to assure meaningful data acquisition. Appropriate solutions are chosen for this purpose.
2. In-house or certified reference materials and reagent blanks are used with each batch of samples decomposed. These are chosen in consultation with the instrument operator and should account for approximately 10% of the samples decomposed. Quality control data relating to accuracy and precision determined with these reference materials are kept by the instrument operator and should be available upon request.

Data Evaluation

1. Duplicate determinations are checked for precision. A discrepancy may be due to inhomogenity of the sample, incomplete decomposition caused by acid-resistant minerals, contamination, loss of instrument control, or dilution errors. Each source of potential problem is investigated. If the problem is identified as one that may have affected all samples in a batch, the entire batch must be rerun. If the problem is clearly identified as affecting only the one sample

it is repeated and the whole batch need not be rerun.

2. Determined elemental values are checked with values obtained by the Screen program to indicate the possible presence of acid-resistant minerals. Pay particular attention to those samples which have been flagged by the sample preparation group as containing undecomposed material after acid digestion. If an inconsistency is indicated the sample is redecomposed using an appropriate fusion method.

3. Evaluation of quality control data is monitored by the instrument operator and kept for the Supervisor's attention.

Screen Evaluation

1. Values obtained with the XRF Screen program are approximate.

2. Check the standard reference materials run with each Screen program to determine the accuracy obtained.

3. Adjust analytical values obtained for each sample using the reference material values. For example, if a SRM containing 800 ppm Ba yields a result of 500 ppm with the Screen program, all Ba screen values should be adjusted by a factor of 800/500 = 1.6 to give a better approximation of the Ba content in the samples near this concentration. **DO NOT** change any values obtained by other techniques.

4. A significant discrepancy exists when the adjusted Screen value is higher than the AAS or ICP result by 20%. Significantly lower Screen values, compared with AAS or ICP results, are brought to the attention of the XRF personnel.

The decision sequence for major element determination in the elemental analysis subsection is summarized in Figure PROT1.

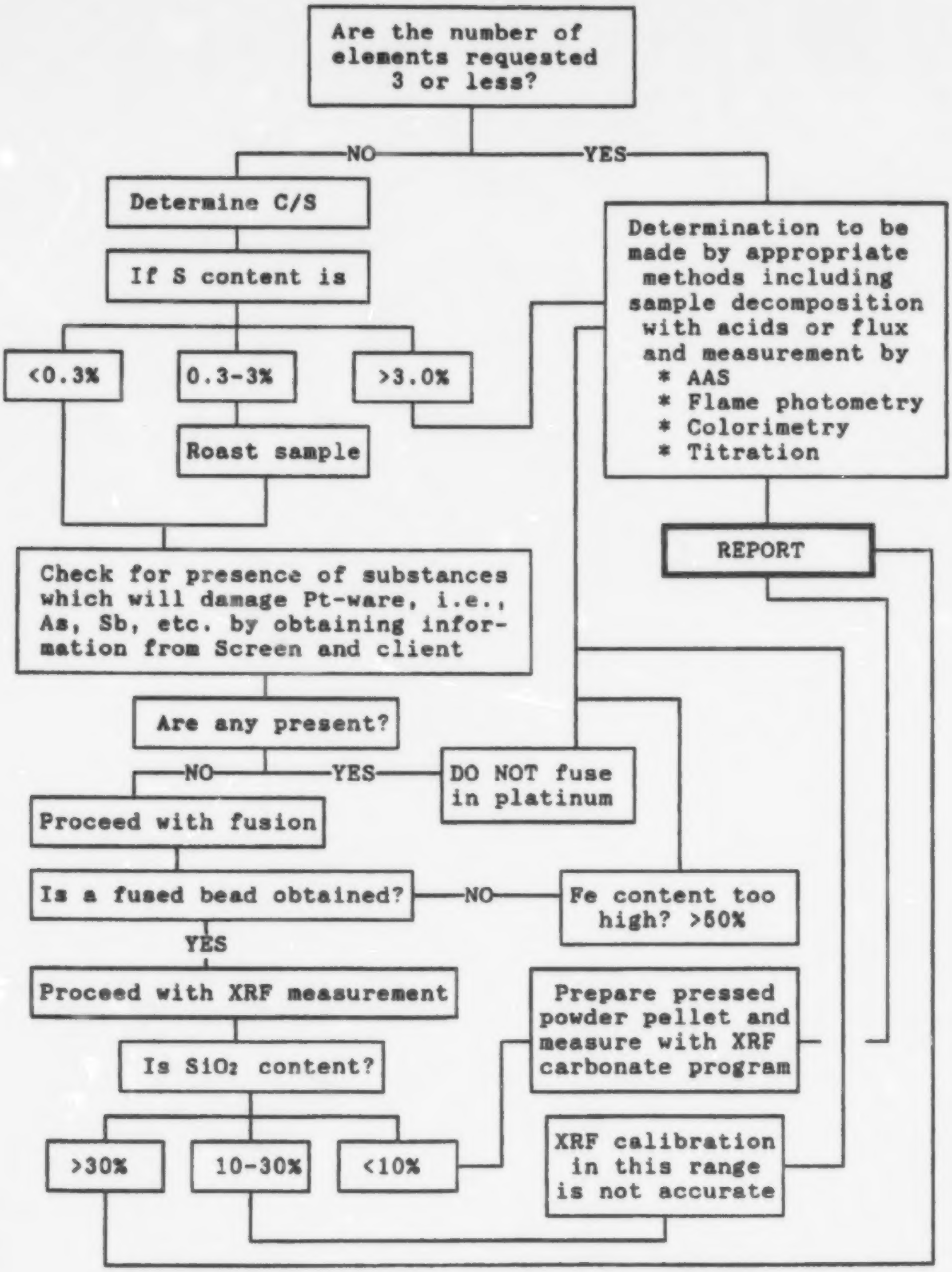
Are the number of elements requested 3 or less?
NO
YES
Determine C/S
If S content is
<0.3%
0.3-3%
>3.0%
Roast sample
Determination to be made by appropriate methods including sample decomposition with acids or flux and measurement by
* AAS
* Flame photometry
* Colorimetry
* Titration
REPORT
Check for presence of substances which will damage Pt-ware, i.e., As, Sb, etc. by obtaining information from Screen and client
Are any present?
NO
YES
DO NOT fuse in platinum
Proceed with fusion
Is a fused bead obtained?
NO
Fe content too high? >50%
YES
Proceed with XRF measurement
Prepare pressed powder pellet and measure with XRF carbonate program
Is SiO2 content?
>30%
10-30%
<10%
XRF calibration in this range is not accurate

Figure PROT1. Decision sequence for major element determination.

SAMPLE DISSOLUTION

Introduction:

The purpose of any sample dissolution technique is to provide a homogeneous solution of the elements of analytical interest. The two most common techniques are acid digestion and flux fusion.

The advantages of acid digestion over fusion include easier operations, less total dissolved solids, less possible introduction of contaminants, and adaptability to the use of robotic systems to perform the digestion. Its main disadvantage is that some minerals are resistant to acid attack, and some elements can be lost in the process.

Fusion techniques are favored when acid resistant minerals are present and total dissolution is vital. The use of fluxes, however, is likely to introduce contaminants as well as providing a solution with high salt content. High salt contents are to be avoided where the sample delivery system can be clogged (ICP nebulizer systems).

A combination of the two techniques can be used for accurate work, but the time required makes its less amenable to batch operations. In this case acid digestion is performed on a sample, followed by fusion of any residue. The solutions are combined to produce a total digestion with minimal salt content.

A list of the more commonly used acids and fluxes is given below.

Acids:

Hydrofluoric Acid:

48% HF (w/w), 29 M is used to attack most silicates. HF will attack glass. **See Safety advisory**.

Perchloric Acid:

60% $HClO_4$ (w/w), 12 M used with HF to decompose silicates and is effective in removing residual amounts of fluoride. **See Safety advisory**.

Hydrochloric Acid:

37% HCl (w/w), 12 M dissolves most oxides, sulfides and carbonates. In combination with nitric acid (3:1) it forms aqua regia.

Nitric Acid:

69% HNO_3 (w/w), 16 M oxidizes organic matter prior to perchloric acid attack.

Sulphuric Acid:

96% H_2SO_4 (w/w), 18 M is used when a high boiling acid is required. Most effective in removing residual amounts of fluoride, but formation of sulfates can create problems with dissolution and with depressant effects during the determination by AAS.

Fluxes:

Lithium Metaborate/Lithium tetraborate:

Used individually or in combination when total dissolution is required. May be used with graphite or platinum crucibles.

Sodium Carbonate:

Na_2CO_3 fused in platinum crucibles is used primarily with classical rock analysis methods.

Sodium Hydroxide:

NaOH or KOH (potassium hydroxide) are used (usually with nickel crucibles) when a strongly alkaline flux is required.

Sodium Peroxide:

Na_2O_2 is a powerful oxidant used to attack spinels, zircon, and sulfides.

Safety advisory:

CAUTION: Exercise extreme care when using any acids and fluxes. Their use should only be attempted after the appropriate **MSDS** sheets have been read and the safe handling and first aid procedures understood. Acids should only be handled in a fume hood with proper ventilation and with proper protective equipment worn. Proper ventilation will be required when handling fluxes which create a dust control problem.

1. **Hydrofluoric** and **perchloric** acids require special care in handling. Hydrofluoric acid (HF) may only be used after training in the proper procedures. Its use is restricted to designated fumehoods. Its hazard lies in the nature of the burn

which can result. Very close attention should be paid to suspected skin contact and treatment applied immediately. **NEVER** handle HF and $HClO_4$ without gloves, proper eye protection, and a lab coat.

2. Non-glass labware must be used when handling HF because the acid attacks silica in laboratory glassware. Perchloric acid may only be used in designated perchloric acid fumehoods with operable scrubbing and/or wash down facilities. Washdown facilities are required in designated fumehoods to prevent the buildup of anhydrous perchloric salts which can become spontaneously flammable. Explosions can result when organic perchlorates are formed. Ensure that organic material, such as alcohols, organic solvents, and paper products are kept away from the digestion area. Organic material in the sample should be oxidized at a lower temperature with nitric acid prior to digestion with perchloric acid.

Decomposition by Acid Attack

Apparatus:

- Top-loading electronic analytical balance, reproducibility +/- 0.001 g
- Polytetrafluoroethylene (PTFE) beakers, 30 ml, 50 ml, 100 ml capacity
- Polypropylene culture centrifuge tubes, 50 ml, graduated every 5 ml
- Disposable polypropylene, culture tubes with caps, 17 x 100 mm, 16 ml capacity
- Hot plates, Thermolyne 12" x 12" or equivalent
- Teflon (PTFE) stirring rods
- Test tube racks
- Polypropylene acid dispenser, 500 ml
- Nalgene graduated cylinders, 250 ml and 25 ml

Reagents:

- Hydrofluoric acid, HF, 48% (w/w)
- Perchloric acid, $HClO_4$, 60% (w/w)
- Nitric acid, HNO_3, 69% (w/w)
- Hydrochloric acid, HCl, 37% (w/w)

Procedures:

1. Sample Preparation for T1 Options and T2 Analytical Package (HNO_3 - $HClO_4$ - HF)

This is a mixed acid attack, generally considered to provide a "total decomposition", and produce a solution for determination of trace elements by AAS or ICP-OES. It is used to break down silicates in rocks, soils, and sediments.

1.1 Prepare an acid mixture to contain 100 ml of $HClO_4$, 50 ml of HNO_3, and 400 ml of HF using a Nalgene graduated cylinder for measuring the HF volume. Store in a clean polypropylene dispenser used to deliver HF acid. (see Note 1).

1.2. Weigh 0.500 g of sample into a 50 ml PTFE beaker.

1.3. Add 15 ml of acid mixture (see step 1.1) to the beaker using Nalgene labware for delivery.

1.4. Ensure complete wetting of the sample by swirling the beaker.

1.5. Place beakers on hotplates at 150°C and evaporate to dryness overnight.

1.6. Gently tap beakers to cause any droplets of acid condensed on the upper portion of the beaker walls to fall to the bottom.

1.7. Leave beakers on the hot plate until fumes cease.

1.8. Check for more droplets and repeat steps 1.6 and 1.7 until acid droplets have been removed.

1.9. To the dry residue, add 2 ml of concentrated HNO_3 and heat on hot plate for 1 minute.

1.10. Remove beaker and add 0.5 ml of concentrated HCl, allowing any vigourous reaction to subside before placing beaker on hot plate.

1.11. Use a teflon rod to break up the residue while adding 15 ml of distilled water.

1.12. Heat on the hot plate for 15 minutes or until dissolution appears complete.

1.13. Examine the beaker for any incompletely decomposed residue and record its presence for that sample. (see Note 2)

1.14. Transfer the cooled solution to a 50 ml polypropylene centrifuge tube and bring to 25 ml mark using distilled water.

1.15. Cover the test tube with parafilm or a cap and mix well.

1.16. Split the solution into two fractions using 17 x 100 mm polypropylene culture tubes for distribution to AAS and/or ICP-OES. (see Note 3)

NOTES:

1. A clean, empty, supplier HF dispensing bottle may be used for this purpose.
2. The presence of minerals resistant to acid attack may be observed at this time. Check determined values against values obtained with XRF Screen and ascertain whether fusion is required for these samples.
3. Dilution factor for these fractions is 50. ICP-OES will dilute their fraction 1:1 using the liquid handling apparatus.

2. Adaptation of Procedure 1 to a Robotic System

The following is a description of the steps taken by a robotic system to provide a final solution identical to that produced by the manual approach given in 1 above.

The system requires a weighed sample to be placed at a **home** position (rack number and position). The PTFE vessels have a maximum volume of 30 ml, can be capped, and have dimensions 65 mm (height) x 29 mm (diameter).

The system can handle 60 samples in two groups of 30. Current programming allows only 48 samples to be processed as one group of 30 and one group of up to 18.

2.1. Sample 1, from rack 1 is moved to the dispensing station and 8 ml of HF, 1 ml of $HClO_4$ and 2 ml of HNO_3 is automatically added, under robotic control, to the PTFE vessel.

2.2. Sample is placed in position 1 on the low temperature hot block, set for 150°C, and allowed to remain there for 3 hours 30 minutes. (see Note 1)

2.3. Sample 2, from rack 1 is processed in the same manner as steps 2.1 and 2.2.

2.4. All samples from rack 1 are treated until the maximum of 30 samples have been placed in the low temperature hot block.

2.5. After sample 1, rack 1 has been in the low temperature hot block for 3 hours 30 minutes, the robot will transfer it to position 1, of the high temperature block 1, set at 180°C. (see Note 2) The samples will remain at this position for 17 hours.

2.6. If sample 1, rack 2 (sample #31) is available, the robot will process this sample as in steps 2.1 and 2.2. This sample is then placed in the vacated position 1 of the low temperature hot block. Time required for this operation is approximately 3 minutes. (see Note 3)

2.7. Operations 2.5 and 2.6 are repeated until all samples originally in the low temperature hot block are now in the first high temperature block, and all samples from rack 2 are in the low temperature block.

2.8. The robot will remove samples from the low temperature block to the second high temperature block after 3 hours 30 minutes has elapsed for each sample. It will remain in a rest position for the full 6 1/2 minutes between samples.

2.9. After sample #1 has been in the high temperature hot block for 17 hours, it is transferred to the acid dispensing station where 2 ml of HNO_3 are added, a 1 minute pause introduced, 0.5 ml of HCl is added, and after a 1 1/2 minutes pause, and 0.5 ml of distilled water is added.

2.10. Sample #1 is placed in the low temperature hot block for 8 1/2 minutes. (see Note 4)

2.11. Time will allow sample #2 to be processed as in steps 2.9 and 2.10.

2.12. Robot initiates next step for sample #1. (see Note 4)

2.13. Sample #1 is transferred to dispensing station where 22.5 ml of distilled water are added to the vessel.

2.14. Sample #1 is transferred to the capping station, vessel is capped and placed in its home position.

2.15. Robot has time to process sample #3 as in steps 2.9 and 2.10.

2.16. Robot must now process sample #2 as in steps 2.13 and 2.14.

2.17. Samples are processed in the above sequence until all vessels have been capped and placed in their home positions. (see Note 5) This completes the decomposition steps handled by the robotic system.

2.18. Capped vessels are mixed thoroughly, and split into two components for distribution to AAS and/or ICP-OES measurement. (see Note 6)

NOTES:

1. The rate limiting time for this initial step is 6 1/2 minutes. Sample 2 will not be processed until this time has elapsed.
2. The robot will note the time remaining of the 6 1/2 minutes before sample 2, rack 1 needs to be removed to the high temperature block. If sufficient time is available to initiate another step in the program before this time has elapsed, it will do so. (see step 2.6)
3. Sample #32 cannot be processed before #2 because of insufficient time (see Note 2) and because only one low temperature hot block is available and position 2 is still being occupied by sample #2.
4. This 8 1/2 minutes is another rate limiting time. Another sample will be processed if sufficient time is available before the next step for sample #1 needs to be initiated.
5. Time elapsed for first sample to complete the process is 20.5 hours; for a batch of 48 samples the time is 24 hours.
6. Dilution factor for these solutions is 50. ICP-OES will dilute their fraction 1:1 using the liquid handling apparatus.

3. Fast Sample Dissolution for T1 Options by Flame AAS (HCl - HF - HNO_3)

This mixed acid attack requires less time to complete than procedure 1 which uses $HClO_4$. It is used for material received and designated as an "assay" sample which require a faster turn-around time and usually fewer elemental determinations with less stringent accuracy requirements. The solution resulting from this procedure is suitable for measurement with atomic absorption only.

3.1. Weigh 0.500 g of sample into a 50 ml PTFE beaker. (see Note 1)

3.2. Add 5 ml of HCl and 5 ml of HF to the beaker, swirling the beaker to ensure complete wetting of the sample. (see Note 2)

3.3. Place the beaker on a hotplate at 150°C and evaporate to dryness (approximately 3 hours).

3.4. Add 5 ml of HNO_3 to the dry sample and evaporate to dryness.

3.5. To the dry residue, add 5 ml of HNO_3 and heat on the hot plate for 1 minute.

3.6. Add 20 ml of distilled water, and using a teflon stirring rod, break up the residue to aid in dissolution.

3.7. Continue to heat on the hot plate for 15 minutes or until dissolution appears complete.

3.8. Examine the beaker for any incompletely decomposed material and note its presence. (see Note 3)

3.9. Cool and transfer the solution to a 50 ml polypropylene centrifuge tube and bring to the 50 ml mark with distilled water.

3.10. Cover the tube with parafilm or a cap and mix well.

3.11. Distribute samples for AAS determination. (see Note 4)

NOTES:

1. If the sample is an ore material or is dark in colour it is advisable to use a 100 ml PTFE beaker.
2. At this stage, if the sample contains sulfides, it will be necessary to add 3 ml of HNO_3 prior to the addition of HF and cover the beaker with a watch glass. Allow the sample to reflux for 15 minutes on a hot plate, wash the watch glass with distilled water and add the HF.
3. The presence of minerals resistant to acid attack may be observed at this time. Check values determined by AAS with those obtained by the XRF Screen Program. The XRF Screen will be available only if chromium or barium have been requested.

4. Dilution factor for these solutions is 100. Acid concentration is 10% HNO_3.

4. Sample Dissolution for the T4 and T5 Analytical Packages

This preparation is a modification of Procedure 1, and requires fastidious attention to detail. It was developed to provide a solution for the determination of rare earth elements and yttrium by ICP-MS. It is the procedure required when ICP-MS is used for analytical measurement. Other elements determined with this solution are uranium, thorium, thallium, hafnium and tantallum.

4.1 Preparation of 10 ppm Ruthenium/ Rhen-ium Standard

4.1.1. Pipet 20 ml of 1000 ppm Ru solution and 20 ml of 1000 ppm Rh solution into a 200 ml volumetric flask, and make to volume with 10% HNO_3. (see Note 1)

4.1.2. Pipet 20 ml of the 100 ppm Ru and Re solution prepared in 4.1.1 into a 200 ml volumetric flask, and make to volume with 10% nitric acid. Store solution in a polypropylene bottle.

4.2. Preparation of mixed acid solutions

4.2.1. Solution **A**: Mix 400 ml of HF, 40 ml of $HClO_4$, and 40 ml of HCl and store in a polypropylene acid dispensing bottle. (see Note 2)

CAUTION: Be aware of the hazards noted at the beginning of this section dealing with hydrofluoric and perchloric acids.

4.2.2. Solution **B**: Add 30 ml of $HClO_4$ and 70 ml of HCl to 380 ml of distilled water and store in a polypropylene acid dispensing bottle.

4.3. Weigh 0.200 g of sample into a 50 ml PTFE beaker.

4.4. Add 12-15 ml of solution **A** to the samples, and swirl the beaker to ensure complete wetting of the sample.

4.5. Place the beaker on a hotplate set at 180°C and evaporate to dryness overnight.

4.6. Gently tap the beaker to allow any droplets of acid condensed on the upper portion of the beaker walls to fall to the bottom.

4.7. Place beaker on hot plate until acid fuming ceases.

4.8. Repeat steps 4.6 and 4.7 until all acid has been removed.

4.9. Add 15 ml of solution **B** to the dry residue, place beaker on the hotplate, and evaporate to dryness overnight.

4.10. Repeat steps 4.6 to 4.8. (see Note 3)

4.11. Add 1 ml of HNO_3 to the dry residue, cool, add 6 drops of HCl (see Note 4), and 15 ml of distilled water.

4.12. Place the beaker on the hotplate, heat, and evaporate to a volume of 10 ml.

4.13. Add 1 ml of 10 ppm Rh/Ru standard solution to a 100 ml volumetric flask using a dispenser calibrated to accurately deliver 1 ml.

4.14. Transfer the sample solution from the beaker into the 100 ml volumetric flask containing the Ru/Re standard, and make to volume with 10% nitric acid.

4.15. Mix well and transfer a portion of the solution to a 17 x 100 mm polypropylene test tube and cap.

4.16. Solution is allocated to ICP-MS for measurement. (see Note 5)

NOTES:

1. 1000 ppm Ru and Rh solutions are purchased from manufacturers supplying plasma standards.
2. A clean, empty, supplier HF dispensing bottle may be used for this purpose.
3. This second evaporation to dryness is necessary to remove the last traces of HF. Without this step, low values for the rare earth elements and thorium will result.
4. If the sample contains high iron, additional HCl may be added to dissolve the iron oxides.
5. Dilution factor for this solution is 500, and contains 100 ppb Ru and Re used in the internal standardization scheme.

6. For accurate work, use this acid attack followed by a fusion of any residue using a miniumum of flux, combine the two solutions, indicate total salt content of solution, and present solution to AAS, ICP-OES, or ICP-MS for measurement.

5. Sample Digestion Requiring the Absence of Hydrochloric Acid (HNO_3 - HF)

This procedure is used when hydrochloric acid will prevent the quantitative dissolution of a required analyte. It can be completed within 6 hours and is used when silver, cadmium, and/or lead (high content) are requested. The resulting solution is suitable for AAS determination only.

NOTE: Preparation 1 with its longer decomposition time may also be used if step 1.10 is deleted, i.e., HCl addition is eliminated.

The presence of hydrochloric acid fumes in the vicinity of the decomposing samples will result in low silver results, caused by the formation of insoluble silver chloride. When cadmium in hydrochloric acid solution is taken to dryness, losses in cadmium have been observed. Lead chloride can form and precipitate if the lead content of the sample is >5000 ppm.

5.1. Weigh 1.000 g of sample into a 50 ml PTFE beaker. (see Note 1)

5.2. Add 5 ml of HNO_3 and 5 ml of HF to the beaker. (see Note 2)

CAUTION: Be aware of the hazards associated with the use of hydrofluoric acid noted at the beginning of this section.

5.3. After any vigorous reaction has subsided, place beaker on a hotplate at 150°C and evaporate to dryness (approximately 3 hours).

5.4. Add 5 ml of HNO_3 to the dry sample and evaporate to dryness on the hotplate.

5.5. Add 3 ml of HNO_3 to the dry residue, heat on the hotplate for 1 minute, and add 15 ml of distilled water.

5.6. Heat for an additional 15 minutes or until dissolution is complete.

5.7. Cool and transfer the solution to a 50 ml polypropylene centrifuge tube and bring to 25 ml with distilled water.

5.8. Cover the tube with parafilm or a cap and mix well.

5.9. Distribute the samples for AAS determination. (see Note 3)

NOTES:

1. The weight of sample may be reduced for samples known to contain high lead; an appropriate final volume of solution is chosen. In these cases the final dilution factor for the solution must be clearly indicated.

2. The addition of nitric acid may cause a vigorous reaction, with the release of large amounts of nitric oxide fumes. If the sample is suspected to contain sulphide material, moisten the sample with water before adding the nitric acid and cover the beaker with a watch glass after the nitric acid has been added. Free sulfur will collect on the surface of the liquid and may remain in the final solution present to the AA spectrometer. Care must be taken to avoid nebulizer blockage.

3. Dilution factor for these solutions is 25. Nitric acid concentration is 10-12%.

6. Ashing and Solution Preparation for Vegetation Samples

This is a two-stage technique: (1) Dry ashing the vegetation material, and (2) Treating the ashed material with mineral acid to obtain a solution for ICP-OES determination of the analytes.

Ashing in a muffle furnace at 500° to 550°C is the technique most frequently used for the decomposition of organic matter. The loss of certain metals (lead, cadmium, mercury, arsenic, selenium) is possible through volatilization, the formation of insoluble silicates, or retention on the ashing vessel. If the temperature for ashing is held at 450°C, volatile metals such as lead, zinc, and cadmium are normally retained. Retention on the ashing vessel is reduced if new vessels are "conditioned" in the muffle furnace at 550°C before use, and kept specifically for ashing purposes.

6.1. Weigh 20.00 g of dry material into a pyrex beaker conditioned for ashing purposes. (see Notes 1,2)

6.2. Position the beaker on a silica tray and place in the cool furnace.

CAUTION: The furnace must be in a vented fume hood. Ensure that no smoke enters the room.

6.3. Set the furnace temperature control at 200°C and allow the temperature to rise. The furnace door needs to be held open a few centimeters to allow air to enter the ashing chamber and the smoke to be vented.

6.4. Raise the temperature of the furnace in 50° increments, once it has reached 200°C, holding each temperature until the formation of smoke has subsided. When an increase in temperature produces no additional smoke, charring is essentially complete and the furnace doors may be closed.

6.5. Set the furnace to 450°C, and complete the ashing for 5 hours. (see Note 3)

6.6. When ashing is complete, allow the beakers to cool.

6.7. Add 3 ml of nitric acid, and using a fine jet of distilled water, wash the sides of the beaker (about 5 ml).

6.8. Heat the beakers on the hotplate, and quantitatively transfer the solution to 50 PTFE beakers. Wash the pyrex beaker with small portions of distilled water and add the washings to the PTFE beaker.

6.9. Add 1 ml of perchloric acid to the PTFE beaker and evaporate the contents to dryness using a hotplate set at 180°C.

CAUTION: Note the hazards associated with the use of perchloric acid at the beginning of this section. (see Note 4)

ATTENTION: At this time it is necessary to prepare a reagent blank and solutions of certified reference materials SO-1, SO-2, SO-3, and SO-4 using procedure 1. **HF is required with these samples**. When appreciable siliceous material is present, e.g., in leaves and stems of plant matter, hydrofluoric acid may need to be added. However, these materials also contain a high concentration of calcium and the formation of CaF2 upon addition of HF will deter dissolution and removal of fluoride. If HF is to be used add 2 ml to the PTFE beaker at this step.

6.10. Remove any acid droplets condensed on the walls of the beakers by gentle tapping of the beaker.

6.11. Replace the beaker on the hotplate until acid fumes cease.

6.12. Check for more droplets and repeat steps 6.10 and 6.11 until all acid has been removed.

6.13. Add 3 ml of HNO_3 to the dry residue, and heat on the hotplate for 1 minute.

6.14. Remove the beaker and add a few drops of HCl, allow the reaction to subside, and add 15 ml of distilled water.

6.15. Heat on the hotplate for 15 minutes or until dissolution is complete.

6.16. Transfer the cooled solution to a 50 ml polypropylene centrifuge tube and bring to the 25 ml mark with distilled water.

6.17. Cover the test tube with parafilm or a cap and mix well.

6.18. Add a portion of the solution to a 17 x 100 mm polypropylene culture tube and issue to ICP-OES for measurement of analyte concentrations. (see Note 5)

NOTES:

1. The sample weight and beaker size depends on the density of the vegetation material. Usually 20 g of sample and 100 ml beakers are used, however, 10 g or 250 ml beakers are alternate choices.
2. New beakers need to be conditioned at least three times before they are used for ashing. Conditioning involves heating the beakers in a muffle furnace at 550°C for three hours and removing the beakers from the furnace to cool. Conditioned beakers are cleaned by adding 1:1 nitric acid to the beakers covered with a watch glass, and allowing the acid to reflux by heating on a hotplate. They are then thoroughly rinsed with distilled water and dried at 105-110°C.
3. The charred material in the beaker may be stirred and left overnight to thoroughly ash the sample.
4. The steps which follow are essentially the same as those used for the T1 options and T2 analytical package (procedure A) but without HF addition.
5. Dilution factor for a 10 g sample is 2.5; for a 20 g sample, 1.25. Nitric acid concentration is 10%.

Decomposition by Fusion

Apparatus:

- Porcelain crucibles (Coors High-Form, 30 ml)
- Graphite crucibles (32x29 mm, 30 ml)
- Zirconium crucibles with covers (Low-Form, 25 ml)
- Magnetic stirrers with teflon stirring bars
- Thermolyne Muffle Furnace
- Fire and heat retardant mittens
- Crucible tongs
- Silica tray
- Nalgene beakers, 250 ml
- Borosilicate glass beakers, 250 ml
- Filtering funnels
- Whatman #41 filtering paper, 12.5 cm
- Top-loading electronic analytical balance, reproducibility +/- 0.001 g
- Volumetric flasks, 100 ml, 200 ml

Reagents:

- Lithium metaborate, anhydrous, $LiBO_2$
- Lithium tetraborate, anhydrous, $Li_2B_4O_7$
- Sodium peroxide, granular, Na_2O_2
- Nitric acid, HNO_3, 69% (w/w)
- Graphite powder

NOTE: Use only Na_2O_2 that is protected by plastic from the metal storage container.

Procedures:

1. Fusion with Lithium Metaborate/Lithium Tetraborate

Lithium metaborate is a suitable flux for rapidly decomposing silicates and oxygen-containing minerals such as spinel, chromite, ilmenite, cassiterite, rutile, zircon, gahnite (Zn-spinel), and other resistant minerals.

The lithium borate fluxes do not damage platinumware if oxidizing conditions are maintained, and allow the melt to be poured from the crucible, either into a platinum mold or into a mineral acid solution. The tetraborate salt is utilized to prepare glass buttons in a platinum mold for presentation to an XRF spectrophotometer. The metaborate flux can be substituted for tetraborate, offers a lower fusion temperature (849°C versus 917°C), and provides a more fluid melt for pouring and consequently less retention of material in the crucible.

Graphite crucibles are normally used when the melt is to be poured quantitatively into a mineral acid solution, typically 4% HNO_3, for presentation to solution-based instrumentation.

The tetraborate salt, with a relatively higher acidity than the metaborate salt, is more suitable for fusions of basic rocks and minerals (e.g., dolomite). For acidic rocks (high silica) the metaborate salt is preferable. Flux to sample ratios are usually 5:1.

1.1. Fusion for determination of Barium and Chromium

This fusion is suitable for barium concentrations of 0.05-40.0 percent and chromium concentrations of 100 ppm to 5.0 percent when determined by AAS. This procedure may also be used on any residue following an acid digestion; the weight of flux being dependent on the amount of residue present.

1.1.1. Weigh 0.200 g of sample into a porcelain crucible. (see Note 1)

1.1.2. Add 1.0 g of lithium metaborate and mix sample and flux with a small teflon coated spatula. (see Note 2)

1.1.3. Transfer quantitatively to a graphite crucible and place on a silica tray. (see Note 3)

1.1.4. Fuse in a muffle furnace for 30 minutes at 1050°C. (see Note 4)

1.1.5. Transfer the molten fusion mixture to a 250 ml Nalgene beaker containing 100 ml of 12 % nitric acid.

1.1.6. Dissolve the sample using a magnetic stirrer and teflon coated stirring bar. Complete dissolution requires about 20 minutes. (see Note 5)

1.1.7. Filter the solution using #41 Whatman filter paper (12.5 cm) into a 200 ml volumetric flask. Wash the filter paper several times with distilled water and make to volume with same.

1.1.8. Solution is sent to AAS for determination of required element. Further preparation for determination will be found in the section "Trace Elements Determined by Flame Atomic Absorption".

NOTES:

1. If the samples contain appreciable amounts of sulphide, weighed samples in porcelain crucibles should be roasted in a muffle furnace at 650°C for three to four hours before mixing with the borate flux. Organic matter should be ashed.

2. For samples known to contain> 30% iron oxide, add about 15 mg of pure graphite powder to the porcelain crucible containing the flux and sample. This will prevent the fused melt from sticking to the bottom of the graphite crucible during pouring.

3. New graphite crucibles need to be conditioned in a muffle furnace at 1000°C for 15 minutes.

4. It is important to maintain the fusion for 30 minutes for barium sulphate to be completely attacked.

5. If the dissolution is not allowed to take place at room temperature, the silica may form polymeric hydrated silicic acid which does not dissolve.

1.2. Fusion for the determination of tin by ICP-MS

Read notes for procedure 1.1 above before beginning. Each batch of samples (15 maximum) must include two blanks and one reference material.

1.2.1. Weigh 0.100 g of sample into a porcelain crucible.

1.2.2. Add 0.300 g of lithium metaborate and mix well with a teflon-coated spatula.

1.2.3. Transfer quantitatively to a small graphite crucible (35mm high x 25mm diameter) and place on a silica tray.

1.2.4. Fuse in a muffle furnace for 15 minutes at 1000°C.

1.2.5. Transfer the molten mixture (red hot) into a 50 ml PTFE beaker containing 25 ml of 10% HNO_3.

1.2.6. Stir for 20-30 minutes using a teflon-coated stirring bar and a magnetic stirrer. (see Note 1)

1.2.7. After dissolution transfer immediately to a 100 ml volumetric flask containing 1 ml of 10 ppm Ru/Re standard. (see Note 2)

1.2.8. Transfer a portion of this solution to a 17 x 100 mm polypropylene test tube, cap, and circulate to ICP-MS for the determination of Sn. (see Note 3)

NOTES:

1. It is important that samples should be stirred and made up to volume immediately to prevent the formation of polymeric hydrated silicic acid.

2. For preparation of 10 PPM Ru/Re see 'Sample dissolution for the T4 and T5 Analytical Packages', Step 4.1. (Page 13)

3. Dilution factor for solution is 1000. Nitric acid concentration is 10%.

2. Fusion with Sodium Peroxide

Sodium peroxide (Na_2O_2) is used to decompose silicate rocks containing spinels, zircons, arsenides, and sulfides, and tungsten, niobium, and tantalum minerals, and rare earth phosphates. This procedure is used primarily when chromium (as chromite) is present at concentrations >5 percent.

2.1. Weigh 0.100 g of sample into a low-form zirconium crucible.

2.2. Add 0.600 g of sodium peroxide and mix by shaking or rotating the crucible carefully.

2.3. Place the covered crucible on a silica tray and fuse in a muffle furnace at 650°C for 10 minutes.

2.4. Remove crucible from furnace and cool.

2.5. Hold the crucible with tongs while cleaning the crucible bottom with distilled water.

2.6. Place crucible and fused contents into a 250 ml beaker and cover with a watch glass.

2.7. Add 50 ml of distilled water and 10 ml of concentrated HNO_3 very carefully.

2.8. Using a hotplate, heat for about 15-20 minutes until dissolution is complete.

2.9. Remove the crucible using teflon-coated crucible tongs and wash the crucible with a fine jet of distilled water, collecting the washings in the beaker.

2.10. Cool and transfer to an appropriate size volumetric flask (minimum volume = 100 ml).

2.11. Submit solution for determination of chromium by AAS. See section "Trace Elements Determined by Flame Atomic Absorption".

GRAPHITE FURNANCE OPERATING PROCEDURE

Thermo Jarrell Ash Video 22E - CTF 188

Introduction:

The following procedure is provided as a guide for graphite furnace analysis (electrothermal atomization analysis). For more specific details refer to the section in the manuafacturer's operation manual concerning each step in the process.

It is also assumed that the following steps have been taken:

> The atomizer cell has been aligned to allow maximum transmission of the light from the hollow cathode lamp. See Section 2.4, page 2-6.
>
> A furnace cuvette has been installed, see Section 3.6.2, page 3-14; and decontaminated, see Section 3.6.4, page 3-17.

WARNING: Ensure "run light" on 188 is off and cell body is cool. This can be monitored by the temperature displayed digitally on the AA CRT.

Safety advisory:

1. Always ensure that the cell door is functioning correctly before applying power to the atomizer.
2. Never look directly at a hot furnace cuvette during atomization without proper eye protection (welders goggles).
3. Never touch the cell head (i.e. to change a cuvette assembly) while the "run light" is on, or severe tissue burns may result.
4. Always ensure power to the 188 control module is off before handling the cell head and allow sufficient time for all graphite such as the cell door, cell body, electrode inserts, cuvette, and associated parts (cell windows, washers, and light baffle) to cool before handling.

"POWER ON" Sequence

To avoid communication errors which may lock-up the AA keyboard, always power up the system in the following order:

1. Water coolant (recirculating pump).
2. Argon gas
3. CTF 188
4. Graphics printer
5. AA
6. Autosampler (if used)

Instrument controls:

Front panel of CTF 188

ESC - Stops the furnace cycle from continuing. The RUN light will go out and the ESC light will stay lit until the furnace cuvette cools below 150°C

NEB AIR -Initiates operation of the vacuum pump for nebulization when aerosol deposition is used.

DOOR OPEN - Opens the furnace cell door for manual pipetting when furnace is cool. Pressing a second time will close door.

RUN - Initiates a furnace cycle. When the FASTAC ADM (Aerosol Deposition Module) is in use, the furnace will continue through the number of heating cycles selected under the MODE Key on the AA CRT. To discontinue the process, press RUN again and the current cycle will be completed and the remaining cycles will not be initiated. Pressing ENTER on the AA keyboard will cancel the remaining cycles.

Right Panel of Video 22E

Most controls are self-explanatory. The following functions should be noted.

SIGNAL/BACKGROUND - selects "hollow cathode" or "D2 arc" intensity reading respectively for both energy and current indicators. In S/H mode, signal selects monitoring of the low current pulse, while background selects monitoring of the high current pulse on energy and current indicators.

HOLLOW CATHODE -lamp current for channel A is controlled from turret, for channel B by small diameter knob at B. Large diameter knob for A and B controls S/H background current.

RESTART/STANDBY -will reset the microcomputer's program counter to 0000 which can correct certain operational errors.

OPERATE -used when entering an analytical program.

HIGH VOLTAGE A/B -sets the photomultiplier voltages for A or B.

Keyboard on Video 22E

INT - used in the flame mode of spectrometer.

READ - initiates integration for flame analysis; **RUN** key on CTF 188 performs the same function for graphite furnace work.

STD - used with calibration procedures.

ENTER - executes the keyed command.

I/O - This key formats the input and output functions of the spectrophotometer.

The CRT displays

I/O:
1 Recorder
2 Printer
3 Serial Port
4 Time
5 Date
6 OpI.D.
7 Wt. Correction
8 Percent Modulation
9 To exit

The following settings should be made after the I/O key is pressed and the above menu is displayed. For example, to choose Recorder, press 1 and Enter. Default choices are indicated by an asterisk "*" and only require the enter key to be pressed to proceed. Once the settings have been made, press I/O to return to the menu and continue. Exit the menu by pressing 9 and Enter.

1 ENTER Enables the formatting of the recorder output. *2 Abs.

Press enter to choose this default setting. Then choose 2 (Element-bkg) from the next menu for corrected absorbance signal. The above process is repeated for Channel B if in two-channel operation (two elements determined simultaneously).

2 ENTER----*Enter Sample no.

When first sample no. is entered, all subsequent analyses will be incremented by one. Auto-zero and auto-cal functions will not increment the sample number. The I.D. of the sample currently being analyzed is displayed on the bottom of the CRT.

1 IBM Compatible

Auto-Graphics

*0 Off - The graphics printer will serve only as an alphanumeric printer. A hard copy of the CRT is made by keying the decimal point on the AA number pad.

1 On - The graphics printer will automatically trigger the CRT graphics after every integration cycle **if peak area integration is selected with graphics.**

*1 All data - provides a hard copy of the CRT each time an absorbance profile is displayed **if autographics was selected.**

2 Stats only - lists sample number and statistical summary; the graphics printer does not hard copy the CRT.

NOTE: Do not take the graphics printer off-line while it is printing; doing so would lock-up the AA's microprocessor.

3 ENTER

*0 Off - deactivates the RS232C interface.

1 On

0 Printer - used to transmit data to an external printer properly configured to accept data.

*1 Protocol - must be entered to use the **ADS-200 system**. Enter default settings from next CRT displays.

CAUTION: If not using the ADS-200 system, do not select the Protocol option; otherwise, the microprocessor locks-up and the message "waiting for RS232C" appears on CRT

4 ENTER Sets the time of day. Enter the appropriate two-digit code when prompted.

5 ENTER Sets the date. Enter the appropriate twoditit code when prompted.

6 ENTER Enter operator I.D. as a two digit code. Key ENTER to cancel I.D.

See Section 3.2.10 of the VIDEO 22E Spectrometer Operator's Manual for further explanation of the I/O key.

AA Spectrometer Keyboard (System Software)

A detailed description of the software menu for each key (Mode, Recall, Store) is provided in the VIDEO 22E Spectrometer Operator's Manual. Default selections are indicated with an asterisk * on the CRT. Press ENTER to select the default condition. To select any of the other options displayed on the CRT, you must press the appropriate key, then key ENTER.

Mode Menu

The Mode menu is used to set the instrument parameters (element, optics, background, results, statistics, atomizer, autosampler, test and exit) for instrument operation.

The following menu should appear on the CRT after the MODE key is pressed.

Mode:

1 Element -
2 Optics - AA, DB
3 Bkgnd -
4 Results - S/E=01.0
5 Statistics - 0
6 Atomizer - CTF
7 Autosampler - off
8 Test
9* To exit

1 ENTER Select element or elements if dual channel is used. Enter element number from the resulting table that appears and press ENTER.

2 ENTER Select optics for each channel if AA, DB is not on Mode menu display.

3 ENTER Display the Background menu and select appropriate background for each channel (D=deuterium arc, S-H =Smith-Hieftje). A two-digit number must be entered; one for channel A, then one for channel B.

NOTE: If D2 background correction has been selected, the CRT will display "D2 Warmup" for a few seconds.

NOTE: To run S-H and D2 simultaneously, enter 4.2 which is S-H in channel A and D2 in channel B. Entering 2.4 is invalid.

4 ENTER Select 1 for Conc. (S/E is scale expansion in absorbance mode). Select *1 Normal. Select default condition 1.1 to display all information (concentration, integration, mode, and concentration of calibration standards) for both channels.

5 ENTER To chose statistics. Enter no. of runs as 3 and ENTER. Select *1 to display Mean, SD, RSD. Note: Selecting 0 or 1 as the number of runs indicates no statistics and 0 is displayed on line 5 of Mode menu.

6 ENTER Chose CTF as atomizer if furnace has not been turned on. AA units will the 188 will default to the mode last used.

7 ENTER Turn autosampler on if required. Further description for autosampler (PS-75 Prep Station) follows.

9 ENTER To exit the Mode menu.

Autosampler with Dilutor

This accessory provides automatic sample dilution, standard preparation, matrix modification, and standard additions preparations fully under computer control via the CRT and keyboard of the Video 22E spectrophotometer.

The Prep Station Option is selected through the MODE key, 7

ENTER

- Select 2 Autosampler with diluter
- Turn on the Sample Changer and Diluter
- Press *1 Prime to prime the syringe and fill
- the rinse station.
- The CRT will display (if AA is in the concentration mode) options for

1 Run samples
2 Calibrate with autosampler
3 Standard addition
9 To exit

Calibration

2 ENTER Change to read 0.0 mls matrix modifier.

Bulk AZ & AC?

BULK VOL.=5.0 mls times 0*

This allows you to prepare large volumes of auto cal solutions. You are given the option of having as many times the previously selected Final Volume (in this case - 5.0 mls) as desired (max. 45 mls) prepared in the AZ and AC vessels. Enter 0 to bypass.

Select *1 YES for rinse between samples.

Select 3 Both for dual channel operation. You are now ready to enter the concentration of the standards through the keyboard.

NOTE: STD C is the autocal standard and should be midrange (0.100 ppm). STD Z must be zero.

NOTE: The highest standard concentration used in channel A is used by the microcomputer to calculate the concentration of the stock analyte which you must prepare and place in the STOCK vessel.

Key in the concentrations for each standard in channel A. When the desired number of standards have been entered, key **STD**. Enter the appropriate concentration for STD C in channel B (0.100 ppm).

NOTE: Enter concentration of STD C to provide three significant figures. Because the PS-75 prepares standards from the same mixed stock solution, entry of the first standard in channel B establishes the other standard values.

The CTR displays a diagram of the sample changer to aid in setup, for example:

```
STK CONC A=          B=
AUTO CAL A= 0.100 B= 0.100
X = SAMPLE/STD       0 = EMPTY TUBE
-------------------------------------
RNS   STK      ---    ***   A/Z  A/C
      row    1 000-- ----- -----
             2 ----- ----- -----
             3 ----- ----- -----
             4 ----- ----- -----
             5 ----- ----- -----
-------------------------------------
LOAD RACK AT THIS TIME
   *1 Prepare
    2 Prepare and Run
    9 To exit
    -*
```

STK CONC's are the concentration of A and B elements in the stock analyte solution to be prepared and placed in the **second large vessel** from the left.

Provide sufficient empty test tube (this example has 3) for standard preparation.

If *1 Prepare is selected, the Prep Station will only prepare the standards.

If 2 Prepare and Run is selected, both preparation and analysis will proceed automatically.

When using the Sample Changer with the CTF 188, do NOT press the escape (ESC) key on the 188 unless an emergency situation requires immediate cooldown of the furnace. If the AA microprocessor locks-up, restart the system by turning off the Sample Changer power, go to RESTART/STDBY on the AA, back to OPERATE, and re-initiate power to the Sample Changer.

NOTE: In the furnace mode, the Sample changer automatically pauses in the "sipper up" position between each sample while nebulizing air for several seconds to clean-out the capillary to the FASTAC.

Once standards have been prepared and analyzed, the CRT displays the calibration curve for channel A. Follow the prompts shown. When channel A has been accepted, the calibration curve for channel B will be displayed.

Run Samples

1 ENTER Change to read 0.0 mls matrix modifier. To use the "manual dispense" mode, enter a value of zero for the Sample Uptake Volume. When prompted for "Dispensed Volume", enter the volume to be placed into each sample test tube. In the "manual dispense" mode, 75 samples can be analyzed. With matrix modification, 37 empty test tubes are required, therefore, 37 samples can be analyzed.

CRT displays options for program to run samples.

CRT displays option for Initial AZ & AC?. NO is normally selected following calibration; YES is normally selected following the recall of a stored calibration curve.

CRT displays Auto Deposit Adjust if FASTAC and concentration mode is being used. If selected the system will automatically cut the deposition time in half for any sample which gives a CONC HIGH reading.

NOTE: Make sure initial deposition time is an even number so the ADA division will not introduce inaccuracies due to arithmetic rounding. For example 6.5 sec would be cut to 3.2 seconds.

CRT continues to display options similiar to those in CALIBRATION above.

Recall Menu

The Recall menu is used to examine calibration curves, instrument conditions, and to review or change furnace methods. The following menu is displayed when the RECALL key is pressed and if CTF is the method of atomization indicated in the Mode menu:

Recall:

2 Instrument Conditions
3 Furnace Method by Element
4 Furnace Method by Matrix
5 Current Method
6 Furnace Curve
9* To exit
-*

2 ENTER Will display the element table. Select desired element and ENTER to display recommended instrument conditions (HCL current, bandwidth, wavelength) which are the same for flame and CTF measurements.

Press RECALL to return to element table. Press ENTER to give initiallization menu for CTF use, then press RECALL to return to Recall menu. A second element may be entered for dual channel use.

3 ENTER Will display available furnace methods for the current element of interest. Select the desired furnace method by typing its repective number and pressing ENTER. The furnace method is displayed on the CRT. At this point if *1 is chosen (Run as is) the analysis will start after the RUN key on the 188 is pressed. Pressing 2 (Change) will allow you to alter furnace parameters, method title, etc. beginning with the matrix name. Once the matrix name is chosen, other parameters can be changed as indicated on the new menu (see below).

4 ENTER Will display available furnace methods for a given matrix to use with a different element. Other options which follow are similar to those when 3 ENTER is pressed.

5 ENTER Assumes you wish to change the furnace paramenters for the current zero method in RAM. This is the method which is in current use or which was used last.

Modifying Furnace Parameters

Modifying Furnace Parameters is reached through options 3, 4, or 5 of the Recall menu. It permits you to alter furnace temperatures, ramp times, hold times, purge flow rates, and integration time for the development of new furnace methods.

Once a desired change is requested by typing its appropriated number from the menu followed by pressing ENTER a new menu will result. The change to be made is indicated by *. The change can be made by typing the desired temperature, etc. followed by pressing ENTER. If no change is to be made at the *, press ENTER to proceed to the next item in the category to be changed. After all stages have been completed the CRT redisplays the modifications.

Purge flow rates are indicated by the following:

0 = stop flow
1 = low flow
2 = medium flow
3 = high flow

If you wish to introduce air (or other auxiliary gas) into the cell body during PYR1, type 1 for YES and press ENTER.

Integration under furnace operation is the time frame during which the absorbance signal is measured by the system microprocessor. In most cases, integration is set to start at stage 4 (Atomization). Make sure peak area has been selected for concentration results and statistics to be based on peak area values. Integration time may be changed next, followed by integration delay time (usually 0.0). The delay time is the time during which the microprocessor waits until beginning the stage chosen for integration. At this stage the **Plot vs Time** selection menu will appear if the graphics option is included. Chose option *2 (default) to obtain a plot of total absorbance (solid line), corrected absorbance (dotted line) and a temperature profile.

FASTAC option permits adjusting of the fastac delay and deposit times once the option has been selected. FASTAC delay is a time period which the sample is allowed to rinse through the spray chamber and then be drawn to waste by vacuum. The recommended time delay is 6 seconds but may vary according to capillary length. FASTAC deposit is the time period during which the sample is drawn through the nebulizer into the cuvette. Higher concentrations require shorter deposit times and vice versa.

The **Furnace Curve** portion of the Recall menu acts as a storage for calibration curves which have been previously stored by the operator and placed in this menu. Storage capacity is 40, numbered 0 through 39. After typing 6 and pressing ENTER the first 10 curves are depicted on the CRT. Further pages can be displayed by pressing ENTER. The desired calibration curve can be displayed by typing the appropriate number (0 to 39) and pressing ENTER. Pressing ENTER again will print the curve. The Recall menu can be displayed by pressing the RECALL key. When a calibration curve is recalled, the printer sample number will revert back to the next sample number that existed at the time the curve was stored. The number displayed with the curve selection menu is the program number associated with the curve. The furnace program is recalled from the RECALL menu.

Store Menu

The STORE key is used to accept (store) newly developed furnace methods and furnace curves. Make sure atomizer is set for CTF (selection 6 of Mode menu). Furnace curves will only be displayed when in the concentration mode (selection 4 of Mode menu).

Back up stored methods with a hard copy using the graphics printer.

If you wish to save a newly developed method you MUST do so through the STORE key while this new method is recognized as the current method (see recall menu), or it will be erased when a new method is selected or developed.

As each new method is accepted, it is assigned the next highest number in the user created series (150 to 349). In addition, you may also overwrite existing methods which you have created . Only the methods created by you can be stored or overwritten. Factor supplied methods can be used to develop new methods but cannot be overwritten.

About Furnace Methods

The 188 microprocessor has an overall storage capacity for 349 furnace methods, divided into two categories of permanent factory supplied methods and storage space for methods developed by the operator. Space allocations are as follows:

- Factory installed methods for ultra-pure water (1 to 52)
- Expansion space for future factory supplied methods for ultra-pure water (53 to 69)
- Factory installed methods for various elements in certain matrices (70 to 129)
- Expansion space for future factory supplied methods (130 to 149)
- Storage and retrieval space for operator created furnace methods (150 to 349). These methods are maintained only if they are stored through the Store menu.

The Store menu is self explanatory. It will prompt you to store a new method in its appropriate space or to overwrite a similar method that you have created but modified. If ENTER is pressed without typing 0 or 1 the initialization menu will appear without storing the method.

To store furnace curves CONC must be selected for the results option of the Mode menu. It is important to **remember that a furnace curve cannot be stored unless the newly developed furnace method it was created for has been stored first**. Furnace curves must have method numbers in order to be recalled by the microprocessor.

NOTE: Furnace curves are temporary unless stored through this menu. Because there is room for only one curve in temporary storage, any curve which has not been stored is erased when a new curve is created.

Selection number 3 (Store Menu), Curve (No CTF), is offered as a method of storing curves without affliation with a furnace method number. It functions exactly as selection 2, except that these curves do not have, and do not require, method numbers because they are stored solely by element.

To **overwrite** a furnace curve, press STORE key, type 2 and press ENTER, and overwrite the desired curve by typing its appropriate number and pressing ENTER. Press ENTER again to overwrite.

Typical Furnace Operation Steps

FIRST Follow the "Power On" Sequence to begin.

SECOND Set the software parameters for furnace operation through the Mode menu. See notes under AA Spectrometer Keyboard (System Software).

NOTE: Set option 3 of the Mode menu first, i.e., single or dual channel, with or without background.

Choose elements (option 3)

Check I/O settings. See notes "Instrument Controls - Keyboard on Video 22E". Make sure Serial Printer is OFF if not using the **ADS-200 system.**

THIRD Set the instrument parameters on the AA spectrophotometer according to conditions stored in the microprocessor memory (Recall Flame Conditions). Set wavelength, bandpass, hollow cathode lamp current, background current. See Section 4.2, page 4-16 of the Video 22E Operator's Manual for insertion and alignment of the hollow cathode lamp.

NOTE: Adjust the PM voltage so that the energy meter is in the green zone. Optimize alignment of the HCL by adjusting the knob located near each spring and by rotating the HCL.

The following is a list of parameters for elements currently being determined by graphite furnace atomic absorption spectrometry.

Element	Lamp Current (ma)	Band width (nm)	Wave length (nm)	S-H Bkg (ma)
Au	5	1.0	242.8	3.0
Pd	5	0.3	247.6	2.5
Pt	5	0.5	265.9	2.5

Background Correction

Smith-Hieftje

See Section 4.4.21, page 4-58 of the Video 22E Operator's Manual. S-H background correction is selected from option 3 of the Mode menu. Set the background current and adjust PM voltage so that the energy meter is in the green zone. Increase Signal HCL current until its energy matches that of the Background.

Deuterium Arc

The intensity of the D2 is automatically set during the autozero routine to match the intensity of the hollow cathode lamp. Select D2 from option 3 of the Mode menu. Key A/Z and READ to allow the D2 arc current to increase until the D2 reference intensity is balanced with the reference (Io) beam of the HCL.

NOTE: In the case of low intensity resonance lines that require upper range high voltage settings, the D2 arc may exceed the HCL intensity, even at the minimum operating current of the D2 arc. In this case, increase the lamp current and decrease the PM voltage, or **insert the D2 arc neutral density filter** into the beam of the D2 arc. See Figure 4-16, page 4-61. Reset the D2 arc by keying A/Z and READ.

NOTE: To switch off the D2 arc, go through the MODE key and press 3 ENTER to change to "A" or "A-bkg (S-H)".

FOURTH Select the Recall menu and call up the furnace method for analyzing the required element/s. Send the furnace method/s to the 188 CTF microprocessor by pressing ENTER. Modify any furnace parameters at this time. Press the RECALL key to display the list of stored calibration curves.

NOTE: If no curves are stored, refer to notes under "Autosampler with Dilutor", Calibration with autosampler.

At this time, return to Mode menu, press 7 ENTER, and select 'autosampler with diluter'.

FIFTH Proceed with calibration if required, or analyse samples. See notes under "Autosampler with Dilutor", 'Calibration' or 'Run Samples'.

Further information can by obtained by referring to section 4.3.3, Calibration Procedure, in the Video 22E operator's manual for creating curves.

NOTE: Under furnace operation the **RUN** key on the 188 is used to initiate the analysis instead of READ.

OPERATION OF THE ATOMIC ABSORPTION SPECTROMETER

Varian AA775

Ensure that the proper instructions found in the operator's manual for the atomic absorption unit have been read. The Varian AA775 is installed with a number of safety features which include:

Burner interlock, preventing the lighting of the flame without the proper burner in place.

NOTE: This system only works if the socket and cable attached to the burner is connected.

Automatic flame shut-down with low fuel rates and when requested by operator. Proper sequence for this procedure is performed.

Flame sensor, to shut off fuel when flame is extinguished.

The general procedures to follow with any atomic absorption unit set up are:

1. Preliminary Safety Check

1.1 Compressed gas cylinders securely fastened.

1.2 Exhaust ventilation fan on and operating.

1.3 Burner head clean and corrected installed.

1.4 Water trap or loop properly filled.

1.5 Adequate supply of compressed gases to complete the task.

2. Parameters to be Set

Parameters are set according to the information recommended by the manufacturer or contained in the information sheets for each element. These are found at the end of each section of this manual relating to determination by atomic absorption. In addition the following optimization procedures should be performed.

2.1 Lamp alignment.

2.2 Instrument gain.

2.3 Burner alignment.

2.4 Flame stoichiometry.

Flames have different temperatures and analytical characteristics, not only because of the gases used but also because of their ratio.

The following guide is used to describe the flame:

Coolest: "reducing" - Fuel rich, luminous, air-acetylene glows bright yellow; nitrous oxide-acetylene a blinding pink-white.

Medium: "stoichiometric" - Balanced fuel and oxidant, air-acetylene has a slight yellow tinge, nitrous oxide-acetylene has about 15 to 20 mm high red feather.

Hotest: "oxidizing" - Fuel lean, air-acetylene is blue, nitrous oxide-acetylene has about 5 to 10 mm high red feather.

2.5 Solution uptake rate.

2.5.1 Adjust to rate of 6 ml per minute if a variable rate nebulizer is used.

2.5.2 Check for blockage in the nebulizer or solution deliver tube.

2.5.3 Check spoiler bead position in bung.

3. Sensitivity Check

The absorbance of a check standard is analyzed and compared with previous data. If the value is within 10% of the mean of previously amassed data the operator can proceed. If not, then optimization procedures should be repeated, or until the problem is found.

4. Calibrate Instrument

Use appropriate standards which encompass the normal range of samples or use the technique of bracketing the sample with high and low standards.

5. Analyze Samples

Reagent blanks, control standards and samples are analyzed. Calibration is checked at intervals. Use a distilled water rinse between samples and standards. Samples with concentrations outside of the calibration limit are diluted to fall within the working range and reanalyzed.

The analytical values are transcribed manually or captured by the instrument microcomputer.

LIQUID HANDLING SYSTEM

A liquid handling system to complement the robotic system used for the decomposition of samples is available for certain applications. The instrument is a **Gilson Model 222-401** and is programmable to perform dilutions, pipetting, dispensing, and partitions or any combination of these. Programs are installed for 1:2, 1:5, and 1:10 dilutions for up to 44 samples using the standard culture tubes. A maximum of 110 samples can be diluted using culture tubes when five racks of test tubes are available The procedures are performed automatically and unattended and are initiated through a keypad although the system may be subjugated to a host computer via an optional interface. Programs can be written according to your needs or existing programs modified.

A variety of test tube racks is available to use with the system. The racks are individually coded so that the probe will find test tube positions. To use a rack of your choice will require extensive initialization for each test tube position.

Four glass syringes (0.5, 1, 5, and 10 ml) covering a range of 2 to 11000 microliters are available. There is a 5 ml and a 10 ml syringe using a piston with a PTFE/ekonel seal for use with acids. The following table shows the performance expected for 5 ml and 10 ml syringes respectively.

Set Volumes (microliters)	**Accuracy %**	**Precision % (30 aliquots)**
5000	0.5	0.05
2000	0.5	0.05
1000	0.5	0.08
500	0.5	0.1
200	1.0	0.2
100	2.0	0.3
50	3.0	0.5
20	5.0	1.0
10000	0.5	0.05
5000	0.5	0.05
500	1.0	0.2
200	2.0	0.3
100	3.0	0.5

With the 5 ml syringe the maximum volume of sample that can be dispensed is 5 ml (sample + diluent). This means that 1:2 dilutions will yield a maximum of 5 ml of diluted solution - 2.5 ml of sample and 2.5 ml of diluent.

<u>PROGRAM FOR 1:1 DILUTIONS</u>
(Stored Under File Number 22)

```
 1  RACK CODE 22/1
 2  INPUT C0/0/1/44
 3  A0=0
 4  FOR A=1/4
 5  FOR B=1/11
 6  A0=A0+1
 7  IF A0C0
 8  HOME
 9  PRINT A0/1
10  TUBE A/B/1
11  HEIGHT
12  ASPIR 0/5/2
13  HEIGHT 70
14  ASPIR 0/4000/5
15  RACK CODE 22/2
16  TUBE A/B/2
17  HEIGHT 120
18  DISP 0/8005/7
19  RINSE
20  DISP 0/2000/9
21  NEXT B
22  NEXT A
23  HOME
```

NOTES: A complete explanation of programming can be found in the manufacturer's User's Guide for 221 and 222 Sample Changers. The above program uses a 10 ml syringe to give 8 ml of diluted sample.

1. A height of 0 is taken as the bottom of the test tube.. Any other height designation is taken as the number of millimeters above the bottom of the test tube, i.e., HEIGHT X sends the probe X mm above the the test tube bottom.

2 Certain coded racks are programmed to work with a designated vertical arm. The Geoscience Laboratories' system is equipped with the 123 mm (standard) length of vertical arm. Code 22 racks are designated to hold test tube of 18 mm o.d.x 150 or 16 x 160 mm. and are programmed for use with the long arm-needle kit (183 mm). At the Geoscience Laboratories, culture tubes are only 100 mm high and can be used with the 123 mm arm since the movement of the probe is not obstructed by the test tubes. Therefore when using racks coded 22, the system assumes you are using the

183 mm arm, and will not accept any height value below 60. This value of 60 must be taken as 0 when using racks coded 22 with the 123mm arm. In the example program above the true height of the probe from the bottom of the test tube is the value given minus 60 mm.

PROCEDURE FOR PERFORMING DILUTIONS

The following dilution programs have been installed for use with a 10 ml syringe:

1:2	dilutions:	File Number 22
1:5	dilutions:	File Number 15
1:10	dilutions:	File Number 110

Instructions:

1. Make sure all tubing, keypad, probe, and syringe are installed correctly (see manual). Place samples into test tube racks such that the y-axis (B in program, maximum 11) is loaded first. Make sure sufficient sample and diluent is available for the complete run.
2. Plug in dilutor and sample changer.
3. Switch on dilutor (Model 401) then sampler (Model 222) in this order, otherwise a message **DILUTOR ABSENT** may appear. Messages **MODEL TEST** and **MODEL 222 V3.O** will appear.
4. Prime the system by pushing **PRIME** on keypad. To stop prime push **PRIME** again.
5. Press **EDIT/SAVE/FILE** key to search for the required file.
6. Press **ENTER** when the required file is found and continue to press **ENTER** until **FILE STORED** appears on display.
7. Press **START** to initiate program.
8. A message will appear on display requesting input of number of samples to be run. Note: Above program is currently set for a minimum of 1 and a maximum of 44.
9. Program will now complete dilutions and return probe to HOME position.
10. When finished wash system out with distilled water by replaced the acid bottle with distilled water and operating the **PRIME** until a complete rinse is accomplished.

THE PHILIPS PW1400 X-RAY FLUORESCENCE SPECTROMETER SYSTEM

Introduction:

The Philips PW1400 XRF spectrometer, a wavelength-dispersive X-ray fluorescence spectrometer, is used to nondestructively analyze the matrix-modified samples. The spectrometer consists of a 100 kV generator with current and voltage stabilization. The X-ray tube is a side-window tube; various tubes with different target materials are available in the laboratory, e.g., rhodium (general use), chromium, molybdenum and tungsten. The maximum power rating of system is 3 kW. The tube system is cooled via a Haskris water chiller.

The system offers a choice of analyzing crystals (up to six mounted on an "assembly"). Crystal positions are:

1	LiF200	(default crystal in parameter set)
2	LiF220	
3	PET	
4	Ge	
5	TlAP	
6	LiF420	

The system has two detectors - a flow counter and a scintillation counter. These can be used individually or in tandem.

The spectrometer is equipped with a microprocessor for control and processing of data. There is a four-position sample holder in the unit. A 72-position automatic sampling device is interfaced to the system. The system can be fed both manually and via the sampler.

The instrument and microprocessor are driven by a Digital Micro PDP Minicomputer with dual disk drive, 10 Mbyte Winchester hard disk using the RSX-11M operating system. Video terminal (with printer for screen dumping) and LA100 Decwriter terminal are both used for either primary system operation and/or secondary result generation. Terminals can be used to access different software routines as long as the same data files are not accessed simultaneously.

Procedures:

1. Turning the system ON

1.1. Confirm that the Haskris Chiller is turned on (water mains must be on). The On/Off switch is flat in the 'On' position and the lights are on.

1.2. Confirm that the supply of clean dry air to the hydraulic system of the spectrometer is connected (gauge should read 60 psi).

1.3. Confirm that the current and high voltage settings on the instrument are set to their minimum values of 20 kV and 10 mA. Settings are controlled from the computer and do not need to be adjusted at the instrument.

1.4. Confirm that the P10 gas and air are turned on: detector gas flow should be at 0.5 l/hr and the capacity should be above 1.0 bars.

NOTE: If tanks are changed or any major change in P10 gas pressure occurs, the gas leak reset button (at the side panel) must be activated before setting-up the instrument.

1.5. Depress the switches for the main and high voltage power located on the upper left corner of the PW1400.

NOTE: If the X-ray tube has not been in use for some time, the tube should be warmed-up (slowly) according to the instructions accompanying the tube.

1.6. Turn the computer on using the I/O switch on the left side of the VT240. This will "boot" the computer into its operational state.

NOTE: If the instrument is on, booting the computer will activate the vacuum pumps in the spectrometer.

2. The Software - Starting the Computer

The operating files (including the RSX-11M operating system) are stored on the Winchester hard disk. The Baud rate on the terminal is fixed at 9600.

NOTE: Commands given by the operator are underlined and are followed by a carriage return [R].

When the computer is turned on, the following message appears at the printer:

```
"KDF11B-BE ROM V0.8"
128KW MEMORY
9 STEP MEMORY TEST
STEP 1 2 3 4 5 6 7 8 9
TOTAL MEMORY ERRORS = 0
CLOCK ENABLED
BOOTING FROM DU0
    (DU0: = Winchester drive)
.....
```

The system continues to transmit messages for some time but these can be ignored by the operator under routine conditions until it prints:

```
>*Time and date (hr:mn dd-mmm-yy
  and RETURN) [S]:
```

2.1. Enter the time and date in the specified format and push RETURN. The system then starts up and requires no input until it requests:

```
ABO -- Task not active
*Should you mount DU1: ?(y/n):N[R]
     (DU1: = disk drive)
*Should you mount DU2: ?(y/n): N[R]
```

2.2. Enter N (as shown above) to both of these queries.

The computer then performs a few more steps, instructs the operator how to use the PW1400 software and logs off, leaving the system in the general monitor system (cursor = >).

The structure of RSX-11M is too complex to discuss in this manual. It should be understood, however, that operating system programs are generally stored in sub-units called directories and are accessed by logging-on. The logging instruction requires both a software name and a password. For the PW1400, the instruction required is: LOG x14/x14.

2.3. Enter LOG x14/x14 and push return. The instrument will respond with:

```
RSX-11M BL35B [1,54] System
RSX11M

dd-mmm-yy hr:mn Logged on Terminal
TT0:  (TT0:= LA100)

Good morning

> ;@LOGIN.CMD

> ;

> ; To run the X14 task, type:
MCR X14 or .X14

> ; To run the Regression task
type: MCR REG or .REG

> ;

> ;@<EOF>

$
```

The new cursor ($) indicates that the system is in the correct directory. Various RSX-11M commands are available to initialize disks, locate directories, etc.

2.4. Activate the system by typing: $ .X14 or MCR X14

The system will respond with a message indicating ownership of software, etc. and ends with the system cursor (*).

NOTE: The PW1400 software operates in two modes: automatic mode (cursor = "*") and manual mode (cursor = "C"). In the automatic mode, the operator can communicate with both the microprocessor which controls the instrument and with the computer which stores the information. In manual mode, the operator can communicate only with the microprocessor.

In order to establish the proper communications between the terminals, the following steps are required:

2.5. At the printer, type ASP (assemble system parameters). There are only two items of interest in the system parameters: the terminal type and whether or not the spectrometer is connected.

The first line will read:

```
TERMINAL TYPE=PR:=
(i.e. waiting for input)
```

2.6. Since the terminal is a printer and this is the default device, simply press return. If the required terminal type is a graphics terminal, simply enter GT.

2.7. Continue depressing the return key until the following message appears:

```
SPECTROMETER CONNECTED = Y := N
```

2.8. Exit the ASP routine by pressing /[R].

2.9. Check the status by typing PSP. If the status is not correct, repeat steps 2.5. to 2.8.

2.10. Exit from the program by typing END. The $ cursor will return.

2.11. After getting the $ cursor type MCR X14 or .X14. This will initiate the PW1400 software.

The ASP program can be used to change the terminal type (PR or GT) at any time.

The system can be run entirely through the video terminal. The screen-dump printer (LA50) can be used to obtain print-out of results (PON = printer on). The printer can be turned on via a switch on the left side.

3. Running the Samples

Once the Measurement Program (MP), Link Program (LP), Rate Correction Set (RC), and the Calculation Parameter (CP) Sets have been defined, it is possible to run samples on a routine basis. The development of these programs is described in the Appendix C following 'Determination of Major Elements - X-ray Fluorescence Spectrometry' (page EA6-6).

It is important to appreciate the manner in which the computer and microprocessor control the instrument and how the operator can control the system. Operator commands to the system software are via three letter acronyms.

Before the spectrometer can analyze samples, it must know what information is required and how the data are to be acquired. After acquisition of data, the computer must know how to process the data to provide corrected results.

Two separate areas, or "memory banks" are used to store this information. These are referred to as the Databank (DB) and the Parameter Bank (PB). Information relating to a particular set of samples is stored under one name that is common in both banks. The Databank provides information that is used by the computer to calculate corrected DATA. The Parameter Bank is used to set the physical PARAMETERS on the instrument so information is acquired in the correct manner.

The information stored in the Databank includes:

- link programs (LP), which "interface" between the measuring program and the calculation parameters (corrections, calibrations, etc.)
- calculation parameters (CP)
- correction parameters (RC) (count-rate corrections)

NOTE: These are all concerned with data processing.

To read what is in the DB type: PDB (Print DATA Bank)

The contents of the PB include:

- listing of channels and channel conditions
- listing of measurement programs, i.e., channels monitored, times used in counting.
- listing of job programs, i.e., sequence of spectrometer instructions.

NOTE: These listings are all concerned with the physical settings of the instrument. They ensure acquisition of data will be carried out in the correct manner.

To read what is in the PB, type: PPB (Print Parameter Bank).

In order to use the X14 program for the analysis of samples, a previously developed Databank must be LOADED into memory. Following this, the associated Parameter bank must be READ into memory.

All trace element instrument parameters are found in Parameter/Databank files labeled OTHER.

Channel conditions for trace elements of interest (stored in OTHER) are listed in the table on the following page.

3.1. Load the required databank: enter LDB XXXXXX. (LDB = Load Databank)

3.2. Read the associated Parameter bank: enter RPB.

The PB read into the microprocessor corresponds to that stored in conjunction with the Databank currently in memory.

ELEMENT		FLT	COL	DET	XTL	ORD	UPL	LWL	KV	MA	ANGLE	+OFFS	-OFFS
Cu[1]	Kα	NO	C	S	1	1	85	15	25	20	45.005		
Rb	Kα	NO	F	S	1	1	75	25	50	40	26.580		
Th	Lα	NO	F	S	1	1	80	15	50	40	27.440	1.80	
U	Lα	NO	F	S	1	1	75	25	50	40	26.125		
Sr	Kα	NO	F	S	1	1	75	25	50	40	25.100		
Y	Kα	NO	F	S	1	1	75	25	50	40	23.755	.60	
Zr	Kα	NO	F	S	1	1	75	25	50	40	22.470		
Pb	Lα	NO	F	S	1	1	75	50	40	40	33.900	.80	
Rh	Kα	NO	F	S	1	1	75	25	50	40	18.300		
Nb	Kα	NO	F	S	1	1	80	15	50	40	21.345		.50
Ga	Kα	NO	F	S	1	1	75	25	50	40	38.845	.46	
Ta	Lβ	NO	F	S	1	1	75	25	50	40	38.465		.30
Ce	Lβ	NO	F	F	1	1	70	30	65	30	71.600		.70
Nd	Lα	NO	F	F	1	1	60	25	65	30	72.125	1.80	
La	Lα	NO	F	F	1	1	70	25	65	30	82.865		1.00
Cs	Lα	NO	F	F	1	1	80	15	65	30	91.865	2.00	

4. Manual Operation

4.1. To store concentration information on the hard disk enter: WDD XXXXXX (Write Data to Disk filename XXXXXX)

4.2. If you wish to print intensity data to the printer as the analysis proceeds, enter: PIN (Print Intensities)

4.3. Place the samples in sampling cups.

4.4. Start the measuring program by entering: SMX (Start Measurement Program). The program will respond with "POSITIONS".

4.5. Respond with: 1 2 3 4 I (Use all four turrets, wait for sample i.d.) The system will bring the first position (#1) into the loading position, open the port and wait for the sample.

4.6. Load the sample into the waiting turret (position #1).

4.7. Type the sample name. Press [R].

4.8. The system will shut the port and bring turret position #2 to the loading position. In case of error (i.e., sample mix-up, no sample, etc.), the instruction can be cancelled by using the /[R] command.

4.9. Repeat steps 4.6 through 4.8. until all samples have been analyzed:

```
"POS # 1 :  " ABC-1234
```

(enter sample numbers)

```
"POS # 2 :  " ABC-1235
```

. . . . etc.

5. Use of Sample Changer

The 72-position sample changer is used to expand the capabilities of the PW1400 as an "unattended" instrument. Samples are loaded in the sample trays (6 samples/tray) and trays are placed in the sample changer. Identification cards are inserted into the appropriate slots of the trays. These cards indicate the tray number and the program (MP/LP) number. As the card is read by the optical reader on the sample changer, the correct measurement sequence will be performed. Samples are identified in the output by the tray number followed by the position number. Samples can be identified in a separate data file (see manual) or samples can be identified using separate lists.

Care must be taken with the automatic sample changer. The plastic trays and identification cards can be sources of poor performance and both should be changed regularly. New supplies should be ordered from Philips Electronics.

5.1. Enter RES (RESET) to clear any previous condititions.

5.2. Enter ASC 20 (Assemble Sample Changer - tray #20)

In this case, the system is informed that tray #20 is the last to be analyzed in the sequence. In some Databanks, MP1 involves the measurement of a Cu blank at reduced power for 10 seconds. By having this sample in the first sample position of tray #20, with the card indicating MP1, the Cu blank is read and the sample changer sequence stops and powers the system down at the end of the run.

The MP to be employed is indicated on the i.d. card, therefore it is possible to run a sequence of samples for different analytical "packages".

5.3. Enter SMX, (this will initiate the analysis).

DETERMINATION OF MAJOR ELEMENTS (M1, M2, M3) X-RAY FLUORESCENCE SPECTROSCOPY

Introduction:

X-ray fluorescence spectroscopy is used for the determination of the ten major elements: Si, Al, Total Fe, Mg, Ca, Na, K, Ti, P and Mn. The results of the analyses are reported as percent oxides. The Philips PW1400 sequential (wavelength dispersive) spectrometer performs the determinations using two analytical programs, one calibrated for a wide range of silicate rocks (M1 and M2 packages), in which the samples are presented as fused glass discs containing about 15% rock pulp, and the other for a range of carbonate rocks (M3 package), in which samples are presented as pressed powder pellets.

In the determination of major elements in silicate rocks (M1 and M2 packages), the sample is matrix-matched by mixing with a heavy absorber, lanthanium oxide (La_2O_3). A fusion with lithium tetraborate flux is carried out. The heavy absorber minimizes the differences in mass absorption (MA) between the samples. For carbonate rocks (M3 package), samples are prepared as rock powder pellets using a boric acid backing. No MA correction is employed in the carbonate rock program.

Geochemical Importance:

Geochemistry deals with two main topics: the composition of the earth and the chemical processes that control the distribution of the elements in space and time. The former is of particular interest to analytical chemists concerned with the analysis of geological materials.

The earth can be divided into zones or shells: the core, mantle, crust, hydrosphere, and atmosphere. The core is approximately 3500 km in radius and is composed of 90.8% Fe, 8.6% Ni, and 0.6% Co which is the approximate composition of iron meteorites. The mantle is about 3000 km thick and is assumed to be composed of mainly peridotite, a rock composed mainly of olivine with some pyroxene, both silicate minerals containing Fe and Mg. The crust is composed of mainly granitic simatic and sialic materials differing in relative proportions in different locations. The term simatic comes from silica and magnesia. Similarly the term sialic comes from silica and alumina. These materials are complex and are not homogeneous. Table MXRF-1 summarizes the approximate compositions of four common rock-types.

The relative abundance of the 14 most common elements in the crust is:

O>Si>Al>Fe>Ca>Na>K>Mg>Ti>H>P>Mn>S>C

The standard classes of rocks are igneous, sedimentary, and metamorphic. As a rough approximation, because the last two classes are derived from the first, the average composition of the accessible part of the crust can be represented by that of igneous rocks.

TABLE MXRF-1.

(Compositions are given in Percent by Weight)

Component	Peridotite	Basalt	Granite	Sediment	Upper Crust
SiO_2	43.9	49.9	70.8	44.5	55.2
Al_2O_3	4.0	16.0	14.6	10.9	15.3
Fe_2O_3	2.5	5.4	1.6	4.0	2.8
FeO	9.9	6.5	1.8	0.9	5.8
CaO	3.5	9.1	2.0	19.7	8.8
Na_2O	0.6	3.2	3.5	1.1	2.9
K_2O	0.2	1.5	4.1	1.9	1.9
MgO	34.3	6.3	0.9	2.6	5.2
TiO_2	0.8	1.4	0.4	0.6	1.6
P_2O_5	0.1	0.4	0.2	0.1	0.3
MnO	0.2	0.3	0.1	0.3	0.2
CO_2	-	-	-	13.4	-

These eight oxides make up 97% of the average igneous rock and eight elements account for 99% of the weight. All other elements can be considered to be 'minor' or 'trace' elements in most rock types.

TABLE MXRF-2. AVERAGE COMPOSITION OF IGNEOUS ROCK

Oxide	Percent by Weight	Element	Percent by Weight	Percent by Volume
SiO_2	59.1	O	46.6	93.8
Al_2O_3	15.3	Si	27.7	0.86
Fe_2O_3	3.1	Al	8.1	0.47
FeO	3.8	Fe	5.0	0.43
CaO	5.1	Ca	3.6	1.0
Na_2O	3.8	Na	2.8	1.3
K_2O	3.1	K	2.6	1.8
MgO	3.5	Mg	2.1	0.3
TiO_2	1.0			
P_2O_5	0.3			
MnO	0.1			
H_2O	1.2			
TOTAL	99.4		98.6	100.0

Safety Advisory:

1. X-rays can cause both somatic and teratogenic damage. It is mandatory that workers wear a dosimeter badge (service provided by Health and Welfare Canada, Health Protection Branch). Pregnant women should not work in the X-ray laboratory.

   Radiation is measured in terms of dose or dose-rate. The unit of biological radiation exposure is the RAD (Radiation Absorption Dose), which is the quantity of radiation dose of any kind (alpha, beta, gamma, or X-radiation), that results in the absorption of 100 ergs or energy per g of biological tissue. The unit of measure of X-ray dose (the radiation given off by a radiation source) is the roentgen (R). The unit of biological radiation damage is the REM (Radiation Equivalent Man).

   The maximum permissable whole-body dose rate is 5 REMs per year or 3 REMs per quarter. This is equivalent to: 5 Roentgens per year, or 100 milliroentgens (mR) per 40 hour week, or 2.5 mR per hour. The maximum permissable accumulated life-time whole-body dose in roentgens is calculated by subtracting 18 from the workers present age and then multiplying by 5. Body parts have associated maximum dose levels. Health and Welfare Canada should be consulted for additional information.

   The spectrometer should be thoroughly monitored with a radiation-survey meter when it is installed, when it is moved and at routine 6-month intervals. The X-ray tube head and specimen area should be monitored each time a tube is changed or if the compartment is disturbed. All monitoring should be done at a strong spectral line of short wavelength (e.g. Mo). The survey meter should be calibrated and sensitive to X-ray energies up to 100 KeV. Readout should be in mR per hour. The meter should not indicate more than 0.5 mR/h at 5 cm from any accessible part of the instrument.

   The instrument is equipped with shielding and interlocks which minimize the possibility of contact with X-rays. The principal sources of exposure are at the interface between the tube head and the specimen chamber, the chamber itself when samples are inserted and removed (there could be leakage from a malfunctioning shutter), and the analyzer crystal which may be exposed during servicing. Leakage is more serious when working at high voltage and current than when working at low energy and intensity levels.

   The primary beam from the tube is very dangerous, generating megaroentgens per minute. Due to the presence of interlocks the possibility of exposure is extremely low.

   The high-potential cable of the instrument (from the generator to the tube) must be secured at both ends. There is still possible danger from high voltage even when the power is off, due to the presence of capacitors in the high voltage circuit.

   Operation and maintenance of the instrument should only be carried out by trained technicians. It is wise to avoid working in close proximity (1-2 meters) to the instrument for long periods of time.

2. Eye protection should be worn and appropriate precautions for open-flame use should be taken during sample preparations.

Method:

The method consists of the following techniques:

1. Matrix modification by either fusing or pressing samples into pellets.
2. Irradiation and measurement of characteristic X-ray fluorescence using a Philips PW1400 wavelength dispersive, X-ray spectrometer.
3. Calculation of final results using calibration curves stored in the instrument's computer.

Samples are either fused with lithium metaborate (silicate rocks) or pressed into pellets (carbonate rocks). The prepared samples are analyzed using an X-ray fluorescence spectrometer. Carbon, sulphur and loss on ignition data must be acquired prior to preparing samples for X-ray analysis.

Apparatus:

- Balance capable of weighing 1-20 g, 0.001 g
- Platinum crucibles (with rim)
  - capacity 27-28 ml
  - weight 40 g
- Platinum molds
  - internal diameter = 40 mm
  - heavy construction, weight = 35 g
- Snap Cap vials (12 dram)
- Triangular support
- Retort Stand
- Meker burner

Additional Apparatus for Automated Procedure:

- LECO FX-200 Fluxer Model 601-600
- Platinum/Gold alloy crucibles: (grain stabilized) 35 mm high x 37 mm ID top x 20 mm ID bottom
- Platinum/Gold alloy casting dishes: (grain stabilized) 30 mm diameter x 8 mm deep

NOTE: Because fused beads are prepared using Pt crucibles and molds, all samples to be fused must be submitted for carbon and sulphur analysis - whether or not these elements are to be reported. If samples are found to contain less than 0.3% S, the samples can be fused without pretreatment. For samples containing 0.3-5% S, the samples are roasted before fusion. Roasting is carried out by placing 1.500 g of the sample in a ceramic crucible and heating in a furnace for two hours, with the temperature increasing from 800-1200°C. The roasted sample is used as indicated in the following section, with appropriate adjustments made in the weight of flux to counteract the effect of the LOI. For samples showing LOI > 10%, the weight of rock powder to be roasted is adjusted prior to roasting such that the weight after ignition is 1.500 g. Calculations for LOI correction of sample material are presented in Appendix A.

Reagents:

- Lithium tetraborate flux
  - anhydrous
  - JMC 99.99%
  - specified LOI <1% @ 800°C
- Lanthanum oxide*
  - Baker >98%, supplied with lot analysis
- Wetting agent: NH_4I

*The lithium tetraborate and lanthanum oxide are purchased in batches and are identified by the manufacturer's batch number. When a new batch is started, it is checked (in triplicate) for LOI and the new blank beads are monitored carefully for contaminants. The LOI should be approximately 0.40% for the flux and 1.30% for the lanthanum oxide. The weight of reagents used in the sample preparation is adjusted on the basis of the LOI data for these reagents.

Procedures:

A complete introduction and detailed description of how to use the Philips PW1400 X-ray Fluorescence Spectrometer system is presented on page EA6-1.

1. Matrix Modification

Samples are prepared for analysis by either pressing into pellets or by fusing the material into glass beads. Silicate rock powder samples are fused into glass beads. Carbonate rock powder samples are pressed into pellets.

1.1. Silicate Rock Analysis: Manual Preparation of Fused Beads

1.1.1. Weigh the following into a snap-cap vial and, wearing gloves, homogenize:

rock powder:	1.500 g ± 0.001 g
lanthanumoxide:	0.887 g,± 0.001 g
tetraborate flux:	7.326 g,± 0.001 g

It should be noted that the weights listed above are based on 'Pure Reagents' i.e., reagents with 0.0% Loss On Ignition. The amount of reagent actually added will depend upon the LOI of the specific reagent batch. For example, typical weights for the lanthanum oxide and flux are 0.918 and 7.355 respectively. The weights are calculated according to the following formulas:

$$Weight\ Flux = \frac{7.326 \times 100}{100 - \%\ LOI\ flux}$$

$$Weight\ La_2O_3 = \frac{0.887 \times 100}{100 - \%\ LOI\ La_2O_3}$$

The final weight of the fused bead should be approximately 9.71 g.

LOI calculations for samples are presented in Appendix A of this document.

1.1.2. Transfer the mixture to a platinum crucible and add a small amount of wetting agent (NH_4I).

1.1.3. Place the crucible in the triangular support on the retort stand and use the Meker burner to heat, on low heat, for 3-4 minutes.

1.1.4. When the iodine fumes have been driven off and the sample begins to melt, place the mold on the crucible and increase the heat.

1.1.5. Periodically during heating, remove the mold and stir the contents by swirling (using Pt-tipped tongs). Replace the mold and continue heating.

1.1.6. When thoroughly molten and mixed, pour the melt into the hot molds. Swirl the melt gently to cover the bottom of the mold.

1.1.7. Allow the mold and contents to cool.

1.1.8. Remove the bead from the mold.

1.1.9. Label the mold with a gummed tag on the upper surface (that is not in contact with the Pt) and place it in a clean sample bag to protect it from contamination.

1.1.10. Crack and re-fuse imperfect beads (uneven thickness, rippled, nonhomogeneous colour distribution).

These beads are now ready to be analyzed by the Philips 1400 XRF spectrometer.

1.2. Silicate Rock Analysis: Automated Preparation of Fused Bead

A Leco FX-200 Fluxer is used to prepare rock powde samples for XRF analysis. Prepare sample/flux/lanthanum oxide mixtures as described in the manual procedure above.

1.2.1. Ensure that crucibles and molds are clean.

1.2.2. Inspect top of burners. If necessary, use the wire brush to clean the burner heads.

1.2.3. Ensure that gas supplies are sufficient and are turned on.

1.2.4. Ensure that the spark electrode and thermocouple have not been disturbed. They should be located 3 mm from the pilot arm.

1.2.5. Turn the fumehood on.

1.2.6. Turn the power switch to the ON position.

1.2.7. Push and hold the PUSH TO IGNITE button until the PILOT LED stays on (20-25 seconds).

1.2.8. Add prepared sample mix to the crucible.

1.2.9. Select the number of burners required by pressing the BURN SEL key the appropriate number of times and finally pressing ENTER.

1.2.10. Determine if the current program is correct by successively pressing the ENTER key to advance through the previously entered steps.

1.2.11. Place the crucibles into the holders and secure them by sliding the sleeve over the rims of the crucibles.

1.2.12. Place the molds in position and press the START button.

1.2.13. When the cycle is complete (3-4 minutes), use the tongs to remove the casting dishes and molds.

1.2.14. Remove the bead from the mold and label it with a gummed tag (on the surface that was not in contact with the Pt).

1.2.15. Crack and re-fuse imperfect beads (rippled, nonhomogeneous colour distribution etc)

Shut-Down:

1.2.16. Turn power ON/OFF switch to OFF.

1.2.17. Turn gas supplies off.

1.2.18. Turn the fume hood off.

1.3. Preparation of Pressed Powder Pellets for XRF Determination of Major Elements in Carbonate Rocks:

Samples of carbonate rock are prepared for XRF analysis as rock powder pellets.

Apparatus:

- Ring press and die (40 mm)
- Aluminum "former sleeve"
- Plexiglass plunger
- Boric acid measuring vial (25 ml)
- Spex pellet press (Model 3624B)

Reagents:

- Boric acid (granular)
- Polyvinyl alcohol (2% w/v in distilled water)

Procedure:

1.3.1. Wearing gloves, weigh 4.0 g ± 0.1 g of -200 mesh rock pulp into a 25 ml snap-cap plastic vial.

1.3.2. Add three drops of polyvinyl alcohol solution (to serve as a binder) and blend into the powder by stirring with a nickel spatula.

1.3.3. Transfer the sample to the 40 mm die to which an aluminum "former sleeve" has been added.

1.3.4. Pack the contents with a plexiglass plunger to form a compact puck.

1.3.5. Remove the sleeve and plunger and add the boric acid powder, placing it on top of the sample. A measuring vial in the boric acid container indicates the amount to be added.

1.3.6. Complete the assemoly of the die and form the pellet by application of 15 tons pressure for 15 seconds using pellet press.

1.3.7. Removed the pellet from the die and label it with a felt-tipped marker on the boric acid side.

1.3.8. Leave the pellet face-down on a cellulose wipe for 24 hours to allow the binder to dry.

A well-made pellet should have no cracks, an even surface and the rock powder should be centered within the outer ring of boric acid (approximately 2 mm). If a pellet is considered unsuitable, a new one is made from a fresh subsample of rock pulp.

It is important to keep the die clean. Boric acid and rock powder can build up on the surfaces and contaminate subsequent samples.

A thorough cleaning with a cellulose wipe after each pellet is removed will generally suffice. Methanol should be used on the wipe to give a more thorough cleaning. The surface in contact with the rock powder must then be treated with care. It can become pitted and must be polished by gently rubbing the surface with a fine abrasive moistened with methanol.

Application and release of pressure on the die-press should be even and slow. The die must be placed centrally and must be level. Failure to do so can result in uneven loading and mechanical failure.

A Philips PW1400 wavelength dispersive X-ray fluorescence spectrometer is used to nondestructively analyze the matrix-modified samples.

A general description on how to use the Philips PW1400 X-ray spectrometer is presented on page EA6-1, and the measurement of trace element analyte concentrations is documented starting on page EA16-1.

2. Calculation of Final Results

All necessary calculations are performed automatically by the system computer.

Major element analysis results are entered on a "Major 1 and Major 2 Analysis Worksheet". The Major 1 (M1) package includes the 10 major components, LOI and a TOTAL. C/S data are normally obtained for M1 samples. The S is required to prepare the sample (roasting etc.). The Major 2 (M2) package includes C/S, H_2O^+, H_2O^-, FeO and LOI in addition to the 10 major components.

The LOI is not included in the TOTAL but is useful for comparing the total volatile content. In this case, the LOI is corrected to account for oxidation of ferrous ion.

TABLE MXRF-3 . RANGE AND PRECISION FOR MAJOR ELEMENT PACKAGES

Component	Silicate Rocks Range %	Silicate Rocks Precision %	Carbonate Rocks Range %	Carbonate Rocks Precision %
SiO_2	30 - 80	0.8	0 - 5	0.2
Al_2O_3	0 - 20	0.3	0 - 3	0.1
Fe_2O_3	0 - 15	0.2	0 - 4	0.02
MgO	0 - 20	0.3	0 - 22	0.2
Na_2O	0 - 10	0.5	0 - 1	0.4
K_2O	0 - 10	0.15	0 - 1	0.02
CaO	0 - 15	0.15	0 - 50	0.4
P_2O_5	0 - 1	0.05	0 - 1	0.02
TiO_2	0 - 3	0.12	0 - 1	0.02
MnO	0 - 1	0.015	0 - 1	0.02
LOI	0.4 - 8	0.4	0.4 - 8	0.4
CO_2	0.1 - 4	0.1	0.1 - 4	0.1
S	0.03 - 2	0.02	0.03 - 2	0.02
FeO	0.2 - 10	0.2	-	-
H_2O^+	0.1 - 6	0.2	-	-
H_2O^-	0.05 - 1	0.1	-	-

During fusion, any FeO in the sample is converted to Fe_2O_3 by the reaction:

$$2FeO + \frac{1}{2}O_2 = Fe_2O_3$$

As the reaction proceeds, the sample gains weight: the weight gained is equal to 0.111 x %FeO.

The true ignition loss, CORLOI, is therefore:

$$\text{CORLOI} = \text{LOI} + 0.111(\%\text{FeO})$$

and is compared to the total volatile content.

The concentration of Fe_2O_3 in the sample is equal to the difference between the total iron measured in the sample by XRF and the FeO contribution.

$$Fe_2O_3 = \text{Total Iron as } Fe_2O_3 - 1.111 \times (\%\text{FeO})$$

Each sample is identified by sample number, batch identifier and batch number. Reports are double checked for agreement in duplicates and totals before being submitted to the Section Supervisor.

Quality Control:

It is important to distinguish between short-term (batch) precision and long-term (multi-year) precision. The Ontario Geological Survey carries out many multi-year projects. The analytical data used in the resulting report can come from rocks collected and submitted for analysis over a period of several years. For the geological interpretations to be significant, they must be based on a realistic evaluation of the long-term precision.

One of the Laboratories blind-duplicate quality control programs involves the insertion of one subsample each, of three in-house reference materials (a granite, a basalt and a syenite), into the routine analytical work on a monthly basis.

It is the precision data from this program that are used to derive our advertised analytical capabilities. The stringency of the test allows us to have confidence that the figures we quote are realistic even if applied to multi-year projects. The rock powder samples are introduced 'blind' into the routine workflow and are subject to no special procedures as often happens when an analyst is aware that QC samples are being run.

Research-grade jobs require precisions to be significantly better than those quoted above. These are achieved by rigorous batch control.

The Laboratories has performed a blind study on in-house basalt and granodiorite standards. The data are produced below and indicate the precision typically to be expected when determined by XRF.

TABLE MXRF-4. IN-HOUSE BASALT REFERENCE MATERIAL (MRB7)

Component	Mean	Precision (2σ)	N
SiO_2	49.14	0.40	15
Al_2O_3	12.65	0.10	15
Fe_2O_3	13.61	0.20	15
MgO	6.13	0.18	15
CaO	9.53	0.08	15
Na_2O	2.45	0.14	15
TiO_2	1.96	0.06	15
K_2O	0.69	0.01	15
P_2O_5	0.25	0.01	15
MnO	0.189	0.005	15
CO_2	0.67	0.02	15
LOI	2.95	0.13	15

Total rock analysis is characterized by an analysis total (including LOI and TOTAL VOLATILES) of 100% for most samples. If the total value lies outside the range 98.5-101.5%, the sample are double-checked. Possible reasons for "poor totals" may include:

- disagreement between LOI and total volatiles
- error in FeO determination
- error in C/S determination
- errors in sample preparation
- high trace element concentrations
- high fluoride
- high sulphur
- high non-carbonate carbon content

Bias can result from such causes as:

- contamination of standards
- contamination or degradation of analytical crystals
- changes in the high voltage power supply or other electronic problems
- detector problems

Certified reference materials (CRM's) or Standard reference materials (SRM's) covering a wide range of element composition are used for the creation of calibration curves. Precision and accuracy are monitored through the use of identified duplicates, blind duplicates, in-house reference materials (MRB 'standards') and SRM's.

TABLE MXRF-5. IN-HOUSE GRANODIORITE REFERENCE MATERIAL

Component	Mean	Precision (2σ)	N
SiO_2	60.52	0.23	10
Al_2O_3	14.83	0.10	10
Fe_2O_3	9.03	0.09	10
MgO	2.76	0.16	10
CaO	3.53	0.04	10
Na_2O	3.27	0.10	10
TiO_2	0.77	0.03	10
K_2O	2.07	0.02	10
P_2O_5	0.18	0.02	10
MnO	N.D.	N.A.	10
CO_2	0.26	0.01	10
LOI	1.72	0.12	10

A comprehensive series of reference rock samples, duplicate analyses, blank determinations and calibration procedures provide the laboratory with sufficient data to assess both the short-term (batch) and long-term (multi-year) precision and accuracy of the data generated. From compilations of large numbers of QC determinations it is possible to outline the long-term analytical capabilities (as advertised in the Laboratories' Analytical Capabilities Document). Determination limits, precision and accuracy capabilities should be checked on an ongoing basis in order to assure quality performance in the laboratory.

Productivity:

A technician should be able to complete 60 samples per day.

Additional Notes:

Some commonly encountered problems and possible solutions are discussed below:

1. Problems with analysis of glass fusion beads.

If the analysis total lies outside the 98.5-101% range, it is important that all parameters are checked.

(a) Check the job sheet and see if the rock-type is unusual. Check the agreement between LOI and total volatiles. Check for high sulphur. See if any trace work has been requested and check trace results for unusually high concentrations.

(b) Check the LOI sheet to see if LOI calculations are correct.

(c) Analyze the obverse side of the bead, or if necessary, crack and refuse. It could be necessary to remake the bead from a new sample of rock pulp.

(d) If LOI and total volatiles disagree, re-do C/S analysis and, if necessary, perform another LOI determination. If C/S and LOI are confirmed, then additional volatiles may need to be determined.

(e) Check the FeO/Fe_2O_3 results. If appropriate, repeat the FeO determination.

(f) If a series of beads are giving problems, it may be useful to check for errors in sample identification or mix-up in samples.

(g) When all else fails, the 'conflicting' elements can be analyzed by classical methods in the chemistry sub-section.

2. Erratic analytical results associated with the XRF spectrometer. Persistent problems should be brought to the attention of the Supervisor and may require a service call.

3. Fused discs containing low (10-30%) silica will produce poor results (below the calibration range of the method). Powder pellets are generally good for silica determinations in the range 0-10%. Thus silica in the range 10-30% is difficult to determine. Classical analytical methods may be used for samples containing this level of silica.

Bibliography:

Mason, B., Principles of Geochemistry, Wiley and Sons Ltd., New York, 3rd Edition, 1966, 329 pages.

Nockolds, S.R., Average Chemical Composition of Some Igneous Rocks, Bull. Geol. Soc. America, V.65.

Read, H.H., and Watson, J., Introduction to Geology, Vol. 1, Principles, MacMillian, 1962.

APPENDIX A
LOI CORRECTIONS

When the sample has substantial loss on ignition, the weights of sample or flux must be adjusted to produce a finished bead of the required weight.

CASE.1: LOI = 2-10% (ADD MORE FLUX)

When the LOI of the rock powder is >2% but<10 %, additional flux is added, equal in weight to the predicted ignition loss of the 1.500 g subsample of rock powder. This ensures that a 100% analysis total still refers to the whole-rock sample, i.e., total bead weight remains the same.

Additional flux weight = 1.500 x LOI(sample)

Analytical results are reported as obtained from the instrument.

CASE.2: LOI> 10% (ADD MORE SAMPLE)

If rock LOI is greater than 10%, it is unlikely that the sample is a silicate rock and that a good analysis will result. If the analysis is carried out in spite of this, then the weight of sample is increased such that the ignited sample weight in the bead is equal to 1.500 g.

Wt. sample = 1.500 x 100/(100-%LOI(sample))

The final analysis total (ca. 100%) will relate to the ignited sample. Results must be factored to relate to the original sample. All concentrations are multiplied by the correction factor:

Correction factor = (100-%LOI(sample))/100

All LOI corrections are noted on the LOI sheet. For CASE.1, the additional flux weight is noted in pencil. For CASE.2, the total weight of rock powder required is noted in red.

Example of LOI corrections:

Base (finished) weight of bead (assuming 0% sample LOI)= 1.500 + 7.326 + 0.887 = 9.713 g.

Percentage of rock powder in bead = (1.500/9.713) x 100 = 15.44%

Example - 1: Sample = 100% SiO_2 LOI = 0%

%SiO_2 in bead = 15.44% equivalent to 100% (rock)

Example - 2: Sample = 96% SiO_2 LOI = 4%

No Correction:

Wt. Si in 1.500 g sample= 0.96 x 1.500 = 1.440 g

Wt. finished bead = 9.713 - 0.060 = 9.653 g

%SiO_2 in bead = (1.440/9.653) = 14.92%
Result expected from XRF analysis = (14.92/15.44) x 100% = 96.61%

Flux correction:

Wt. Si in 1.500 g sample= 0.96 x 1.500 = 1.440 g

Additional wt. flux used = 0.06 g

Wt. finished bead = 9.713 g

%SiO_2 in finished bead = 14.83%

Result expected from XRF analysis = (14.83/15.44) x 100% = 96.02%

Example - 3: Sample = 85% SiO_2 LOI = 15%

No correction:

Wt. Si in 1.500 g sample= 0.85 x 1.500 = 1.275 g

Wt.finished bead = 9.488 g

%SiO_2 in finished bead = 13.44%

Result expected from XRF analysis = (13.44/15.44) x 100% = 87.03%

Sample weight correction:

Wt. sample used = (100/85) x 1.500 = 1.765 g

Wt. Si in 1.765 g sample = 1.500 g

Wt. of finished bead = 9.713 g

%SiO_2 in finished bead = 15.44 %

Result expected from XRF analysis = 100% before correction factor

After application of factor (85/100), result = 85%

APPENDIX B

METHOD DEVELOPMENT

Setting Up a Routine Analysis Program - Majors

This section is included to illustrate some of the methodology that has been used to develop the routine methods. A knowledge of these procedures will enhance the operator's ability to perform accurate routine analysis.

Establishing the Parameters

Creation of the various "banks" and indication of how to use instructions is illustrated through the example of setting up a routine analysis program.

The example shows the process from an empty disk, an empty parameter bank and no data bank.

Turn computer on - MCR X14 as outlined in EA16.

Select the appropriate communications (i.e., terminal at printer, etc.). The system should be in automatic mode indicated by cursor (*).

A. Creation of the Databank, "MAJORS":

Enter *WDB MAJORS

B. Creation of the Parameter bank (PB):

The first information to be entered in the PB are the measuring conditions for each of channel or analyte element. This can be done in either manual or automatic mode. The example shows the assembly of the iron channel.

Enter at the cursor *ACH (Assemble CHannel). The system will respond with

```
NAME:  := FE
```

Enter the required symbol, e.g. type FE, as above. The system will respond with:

```
LINE:KA  := [R]     (default = Kα = K alpha)
```

Enter [R] to select K alpha default value. The system will respond with:

```
FLT: NO   := [R]     (filter Y/NO:   default = NO)
```

Enter [R] to select no filter. The system will respond with:

```
COL:F  := C     (collimator fine (F) or coarse (C))
```

Enter C to select coarse. The system will respond with:

`DET:FS := [R]` (detector: F = flow, S = scintillation, FS = tandem)

Enter [R] to select tandem. The system will respond with:

`XTL:1 := [R]` (LiF200 default)

Enter [R] to select the LiF200 crystal. The system will respond with:

`ORD:1 := [R]` (order of line)

Enter [R] to select the first order. The system will respond with:

`UPL:0 := 80` (upper limit on window of pulse height distribution - PHD)

Enter 80 to select the upper limit on the window of the pulse height distribution. The system will respond with:

`LWL:0 := 15` (lower limit on window of pulse height distribution - PHD)

Enter 15 to select the lower limit on the window of the pulse height distribution.

In order to assemble a channel, typical UPL and LWL values can be assumed. Values can be reset after PHD analysis.

The system will respond with:

`KV MA:0 0:= 60 50` (kV, Ma desired)

Enter 60 50 to specify 60 kV and 50 Ma. The system will respond with:

`ANGLE :0 := 57.470` (enter 2-theta angle)

Enter 57.470 to specify the 2-theta angle. The system will respond with:

`+ OFFS:0 := [R]` (off-set on high angle side)

Enter [R] to specify 0 offset on the high angle side. The system will respond with:

`- OFFS:0 := [R]` (off-set on low angle side)

Enter [R] to specify 0 offset on the low angle side.

If you wish to subtract background from the peak at angles on either or both sides of the peak, the offset values +OFFS or -OFFS are entered as the number of degrees above or below the peak, not the actual 2-theta of the background.

NOTE: Any time the operator wishes to interrupt this or any other routine, type a slash followed by a return (/[R]). For example, when the prompt gives a +OFFS and the operator does not want any offsets, a "/[R]" will exit the operator from the ACH routine.

To change a channel parameter for an element already on file, the operator enters:

ACH FE

and values given as defaults will be those entered previously. To change a parameter, the new value is typed in. Once an element has been entered into the table, it cannot be removed. One way to deal with unwanted channels is to rename them using a nonsensical symbol, e.g., XX, YY, ZZ. As new channels are required, these channels can be renamed.

To see the conditions established for any specific channel, the instruction is:

PCH FE

The system will respond with:

ELEMENT	FLT	COL	DET	XTL	ORD	UPL	LWL	KV	MA	ANGLE	+OFFS	-OFFS
FE Kα	NO	C	FS	1	1	80	15	60	50	57.470	.00	.00

To see all conditions for all channels in the parameter bank, enter the instruction: PCH . The system will respond with:

ELEMENT	FLT	COL	DET	XTL	ORD	UPL	LWL	KV	MA	ANGLE	+OFFS	-OFFS
Fe Kα	NO	C	FS	1	1	80	15	60	50	57.470		
Al Kα	NO	C	F	3	1	75	25	40	75	144.540		
Ti Kα	NO	C	F	1	1	75	25	40	75	85.925	.80	
Mn Kα	NO	C	F	1	1	80	15	60	50	62.950		.80
K Kα	NO	F	F	1	1	75	25	60	50	136.730		
Ca Kα	NO	C	F	1	1	75	25	40	75	113.085		
Si Kα	NO	C	F	3	1	75	25	60	50	108.670		
Na Kα	NO	C	F	5	1	75	25	40	75	55.080		1.00
Mg Kα	NO	F	F	5	1	75	25	40	75	45.225		1.00
P Kα	NO	C	F	4	1	80	15	40	75	140.935	1.00	

It is useful to include in each parameter bank assembly, the following channels for instrument check:

ELEMENT	FLT	COL	DET	XTL	ORD	UPL	LWL	KV	MA	ANGLE+OFFS-OFFS
Cu[1] Kα	NO	C	S	1	1	85	15	25	20	45.005
Al[1] Kα	NO	F	F	3	1	75	25	25	10	144.620

Optimization of channel parameters

Angle Calibration

Once a channel has been defined, parameters can be optimized. A sample containing a high concentration of the analyte is used for this purpose.

There are four sample positions in the changer, 1 2 3 & 4, of which two are of interest, the LOADING and the MEASURING. To load a sample into a specific location, the instrument sample holder must first be brought into the loading position:

Enter SLP 1 (Sample Loading Position 1). This will bring sample location (1) into the loading position.

Place a sample cup containing an appropriate sample into the sample chamber.

Bring sample location #1 into the measuring position by entering SMP 1.

To optimize the ANGLE, the instrument is first set at the appropriate channel (e.g. Fe).

Set the spectrometer to the appropriate channel by entering SCH FE (Set channel)

This will set the correct conditions for Fe measurement.

To calibrate the peak position, the system will perform a short scan around the 2-theta angle listed in the PB. The instrument will determine the "true" peak position.

Enter CAN FE (Calibrate ANgle Fe). The system will respond with:

`TIME: 1.0:= [R]` (count time per point = default 1 s)

Enter [R] to select the default

`RANGE: 0.2:=` (±0.1 degree around the 2-theta entered (in 0.005° steps))

The system performs the scan, finds the new peak and reports both the original and the new peak positions. The message ends with a request to save the new angle (default = yes): [R] saves the new angle; NO rejects the new angle. The new angle is automatically stored in the parameter bank.

Optimization of Channel Parameters

PHD Selection

Window selection can be upgraded by PHD analysis.

PHD FE

The system responds:

```
WINDOW:5    :=    (5% window default - 2% often used)

TIME:  1    :=    (time at point = 1 s)
```

NOTE: If PHD is done in manual mode, the output is a numerical listing of counts. If PHD is done in automatic mode, a graphical display is output.

Select or confirm UPL and LWL settings and if necessary, enter new values in the PB using the ACH mode. To obtain total counts in window selected previously, run PHD and after the first line has been printed, type /[R] to stop.

Storing Parameters

After all channels have been entered, they are automatically stored in memory at the microprocessor. To store them on the disk (under the same name as the databank) type

DPB

For initial storage, the system may ask for FILENAME, to which the DB name is given. In this example, the instruction DPB creates (or updates) the file MAJORS.PBK.

APPENDIX C
SETTING UP AN ANALYTICAL PACKAGE

Once a series of element channels has been established in the Parameter Bank, they should be combined into an analytical package. This requires the construction of various programs:

MP = measurement program
LP = link program
CP = calculation parameters
RC = rate (count) corrections

The Measurement Program (MP)

The measurement program controls the actual acquisition of counts, i.e., channels to be counted, counting time, counting mode, etc., and contains the following information:

- Mask used (aperture); (1 = large: 2 = small)
- Count mode; absolute counts or ratio
- Channels and count times

The Measurement Program is stored in the Parameter Bank and there may be up to 63 such programs in any PB. It is therefore important to keep track of program numbers (identifiers).

For example, if the majors package were to be assigned to measurement program #1 in DB/PB MAJORS, then the instructions would be:

```
AMP 1

MASK     = 1: = [R]               (default = 1)
ABS      =   YES: = [R]
CHAN     PT       PC
```

CHAN refers to the name of the channel to be measured. This can be either a true analyte channel, a background or offset, Compton line, etc.

PT refers to the counting time in seconds.

PC refers to the maximum number of counts desired: generally this is left to its default value, i.e., no count limit: 0E0.

For the MAJORS, the program includes counting at all major element channels and the offset positions for Mn, Ti, P, Mg and Na. Counting times for elements range between 20 and 40 seconds, whereas offset positions are counted for only 10 sec.

```
MASK    :    =  1: = [R]
ABS     :    =  YE: = [R]
CHAN    PT          PC
        0       0E0 : = K 40
        0       0E0 : = Fe 20
        0       0E0 : = Mn- 10
        0       0E0 : = .......entering all channels
        0       0E0 : = .......
        0       0E0 : = Na 40  (last channel)
        0       0E0 : = /[R]
```

The final MP should look like the one printed below (and accessed from the computer by instruction PMP 1).

```
PMP 1
MP 1
MASK     :   1
ABS      :   YE

CHAN     PT      PC
   K     40     0E0
   Fe    20     0E0
   Mn-   10     0E0
   Mn    40     0E0
   Ti    40     0E0
   Ti+   10     0E0
   Ca    20     0E0
   Si    40     0E0
   Al    40     0E0
   P     40     0E0
   P+    10     0E0
   Mg-   10     0E0
   Mg    40     0E0
   Na-   10     0E0
   Na    40     0E0
```

When a measurement instruction is given, the system will slew to the K position (first channel on list), count for 40 seconds, then continue on the Fe position. If there is more than one sample in the turret, each sample will be measured at the K channel first, before changing to the next channel.

If the operator wishes to see the raw intensity counts, the instruction PIN (= Print Intensity) should be entered before the measurement instruction is given.

Rate Correction

The MP for the major elements shown above allow for background correction using the offset position. This is only one of the ways in which the count data can be corrected or adjusted. The three principal rate corrections that can be applied are:

- subtraction of a constant count rate
- subtraction of count rate taken at an offset position or at any other channel position (interference)
- ratioing to count rate at another channel

The RC Table

If the count rate at any given position (channel) contains a "constant" contribution from the spectrometer background, sample cup, additive to sample, etc., this contribution can be subtracted from the observed (raw) count rate before other corrections are made to it. This is done in the RC (Rate Correction) Table under the column BKGR.

The RC table is also used to control contributions to peak count from other channels (analytes) or background. The contribution from the various channels should be identified independently before filling in the RC table. The coefficients used in the correction are entered in the table as 'L' factors. Up to four such corrections can be applied to a single channel.

Examples are shown below:

Example (1) Peak - Background:

Both channel offsets and independently defined channels can be used to define a peak background. All or part of the counts at the background position can be subtracted from the peak counts to give a net (P-B) count rate. This is useful for samples where differences in the background can contribute strongly to the peak count rate. If the background is not totally flat, a background correction factor can be applied. For example, to determine background contributions for a given combination of trace elements using a single background position, a quartz pellet is run as a blank, and raw intensities printed out. Background correction factors, defined as

[CPS(analyte)]/[CPS(background)]

are calculated and entered as the L values in the RC table.

Example (2) Interference Correction:

The regression package of the PW1400 uses "alpha" factors to account for and correct inter-element effects. This requires that the interferent channel be both measured and calibrated. The alpha correction uses the concentration of interferent to make the correction. This is effective for small interferences. Gross interferences caused by direct line overlaps should be accounted for by

- selecting an alternate line for the interferent,
- running a sample containing a high concentration of interferent and no analyte; calculation of net counts at the analyte position; calculation of ratio of net analyte CPS to raw CPS at the interferent channel to obtain the correction factor, which is then entered as the 'L' value in the RC set.

If different measurement programs and link programs (see later) are stored in the same PB/DB combination for varying combinations of a group of elements, the same background positions and RC files can be used to build the link programs.

The RC table for the major elements (under DB MAJORS) is constructed as follows: 90% of the counts observed at the offset position is chosen (arbitrarily) as the background counts for the five elements concerned.

To assemble a correction set:

ARC 1

BKGR: : = [R]
CHL1: : = Ti+
L1 : : = 0.9
CHL2: : = /[R]

This must be repeated for each set of correction factors. To see a specific entry, the instruction PRC # is given, where # is the number desired. To see the entire table, the instruction PRC is given to get:

NR	BKGR	CHL1	L1	CHL2	L2	CHL3	L3	CHL4	L4
1	0	Ti+	0.9000		0.0000		0.0000		0.0000
2	0	P+	0.9000		0.0000		0.0000		0.0000
3	0	Mg	-0.9000		0.0000		0.0000		0.0000
4	0	Na	-0.9000		0.0000		0.0000		0.0000
5	0	Mn	-0.9000		0.0000		0.0000		0.0000

Internal Ratios and Mass Absorption Corrections

To account for mass absorption effects between samples, several methods are used, i.e., ratioing of analyte counts to background and Compton scatter peaks.

For example, if the MA of a particular standard reference material is known from major element contribution calculations, then the MA of an unknown sample can be approximated as follows:

if

MS = MA standard
MU = MA unknown sample
RS = cps at reference peak for standard
RU = cps at reference peak for unknown sample

then

$$MU = \frac{(MS)(RS)}{RU}$$

The net intensity observed at the analyte channel for the unknown sample can be corrected for MA effects, by multiplying by a factor, i.e.,

$$I' = \frac{IU \times MU}{MS}$$

where I' = MA-corrected net intensity
IU = net observed intensity

This, in turn, is equal to:

$$I' = \frac{IU \times MS \times RS}{MS \times RU} = \frac{IU \times RS}{RU}$$

Since RS is expected to be constant, the MA-corrected intensities are expected to be proportional to IU/RU, where RU can be the counts at either a background position or at the Compton scatter position. The latter generally gives the better results.

NOTE: There is a program for Apple IIe comparing the background, Compton-scatter and major element computations of MA value. Application of this program to results observed for a series of reference materials indicate that MA's obtained using Compton-scatter intensities are generally closer to those obtained from major element computations. The Compton scatter peak for the rhodium tube is therefore generally defined in the trace element channel sets as Rh and appears in many measurement programs as the internal ratioing element.

The Link Program

The Measurement Program results in the production of intensity (count) data. The Link Program (LP) "links" this raw data to correction and calibration parameters in order to correct and convert the counts to concentration units. The LP, which is stored directly in the Data Bank (as opposed to the MP which is stored in the Parameter Bank), is generally assigned the same number as the MP from which it receives the data.

In order to assemble a LP:

ALP 1
NEW LIST (for LP not in memory)
NRCH = 0 : = 5

NRCH refers to the number of channels which are to have count correction applied to them. This count correction can be in the form of background substraction, internal standardization, etc. In the example of the creation of the MAJORS package, there are 5 channels which will receive offset correction.

```
OPTION=  0:= 6
```

OPTION refers to one of several data options including entry of external data, dilution factors, analysis totals etc. Option 6 gives the analysis total.

```
MBNR =  0 := [R]
```

MBNR = Monitor Buffer number. If a monitor buffer is used to store counts, with or without ratioing to a buffer to correct for drift, the number should be entered here. If the buffer is not used, leave MBNR = 0. The application of monitor buffers is explained in the software instruction manual.

```
INT. RATIO = NO := [R]
```

INT. RATIO = internal ratio to the counts appearing at one of the channels measured. If ratioing to background, the Compton-scatter peak or any true internal standard element is required, then Y is entered, and the system requests identification of the internal standard channels (up to three). It should be noted that only "real" channels can be used for internal ratio. Off-set channels, e.g. Ta- or Ga+ cannot be used.

```
MNR =0 : = 1
```

CPNR = calculation program (calibration coefficient file). Although any number can be used in this file, it is probably better to use a CP file of the same number as the LP and the MP.

```
DLST = 0 : = [R]
```

MODLST = moduli list = combination channel results and factors to provide some additional calculation or ratio or a specific application. In this example, the value is left at the default of 0.

```
CHAN    RC    IR
```

At this point in the assembly, the channels (CHAN), the rate correction number (RC) and the internal ratio (standard) channel (IR) are specified. Since there can be up to 63 RC factors, the ones desired must be chosen carefully.

For example:

```
ELMNT    RC    IR:   := Ti 1 [R]
ELMNT    RC    IR:   := P+ 2 [R]...
```

If an internal ratio were required, the channel on which the ratioing would be calculated is entered following the RC number. As soon as the number of entries is equal to the NRCH defined previously, the system returns to the cursor.

Calibration

Major elements are calibrated using a series of certified reference materials (CRM's) whose element concentration values cover an adequate range for the rock type being considered (i.e., silicate or carbonate rock). A regression file is prepared which contains the concentrations and observed intensities for the series. The following example illustrates the steps required. The measurement program is assumed to be MP 1.

Acquiring the Intensities

The following commands are made on the assumption that the appropriate measurement and link programs are available (along with the RC correction set).

SPR 1 - This command (start prepare regression) instructs the system to run samples and to store the data in a regression file.

"FILENAME" MAJORS - Regression file to be created = MAJORS.R01

"SAM POS" This command is common to all instructions operating the spectrometer. It asks the operator to identify the turret positions for the SRM's. The response is given as the turret numbers separated by spaces; in order to introduce sample (SRM) identifiers, the response is followed by an I.

```
1 2 3 4 I
```

The sample holder (turret) then puts #1 into the loading position and opens the port. The system prints:

```
SAMPLE #1 :
```

and awaits the entry of the sample name. The sample is placed in position, the name is typed at the terminal and upon receiving a carriage return, the port closes and the system puts #2 into the loading position. When all the positions specified earlier are filled, the system begins to measure X-ray intensities according to MP1. Intensities are stored automatically under file MAJORS.RO1. (XXXXXX.RYY where XXXXXX = file name, YY = Measurement Program Number). Additional reference materials can be run in a similar manner.

Entering Concentration Data

Once all intensities have been measured, the intensity file is opened and the accepted (literature) concentration values are carefully inserted into the file. (Every time the operator wishes to manipulate a data file, it must be opened using the instruction illustrated below).

```
OPF MAJORS.R01
```

The system responds with file information, ending message with cursor.

`ACD` (= Assemble concentration data)

The system then asks the operator to input concentration data of the elements in the order specified in the MP/LP set for the standards (in the order stored in the regression data file). The Philips software is set-up generally to handle concentration units in percentages. Trace element values can be entered for convenience as ppm/1000. Thus, for example, a value of 125 ppm would be entered as 0.125. Care must be taken with interpretation and reporting of data.

If the operator wishes to stop entry at any point, he/she types "/[R]" (slash/return). One can re-enter the ACD routine at any SRM, e.g., ACD 4 enters the routine at the fourth SRM.

To view the total concentration file, the operator types

PCD (= Print concentration data)

when finished, the file is closed,

CLF (= Close file)

Regression

After all intensities and concentrations are entered into the MAJORS.R01 file, the regression is performed. To do this, the operator leaves the X14 software (by typing END), and enters the regression software (MCR REG). The system requests the regression filename. The response is the data filename MAJORS.R01 (or file required).

For theories on the interpretation of XRF data the reader is referred to R.H. Jenkins and B. DeVries, "Worked Examples in X-ray Spectrometry", Springer Verlag, New York, 1970.

The default calibration procedure is the De Jongh model (DJ) which is a concentration-based correction model. The general formula is

$$C_i = (D_i + E_i R_i)\,(1 + \sum \frac{a_{ij} C_j}{100})$$

where

C_i = concentration of analyte
R_i = intensity of analyte
E_i = slope of calibration curve
D_i = intercept of curve
a_{ij} = alpha coefficient for interferent j
C_j = concentration of interferent j

This formula is similar to the Lachance-Trail model, but corrects for self-absorption. It is used extensively and has proved successful for most applications. Constants D and E are instrument dependent; alpha coefficients are fixed and known for any sample/spectrometer combination and can be input from tables or calculated during the regression procedure.

After signing on the regression software, the system waits for instruction

SRI = start regression input

```
MODEL = DJ : =  [R]  or DJ
LOAD ALL ELEMENTS = YE: =  [R]
LOADED ELEMENTS: SI AL FE.....
10 OF THE 10 SAMPLES LOADED(inform operator of the number of standards in the file)
REGR. ELMNT : =  SI        (input element of interest)
```

To calculate the D and E values, the operator types:

SRA

and the system responds:

```
ELEMENT = SI   MODEL DJ   SIGMA = 0.01039  K = 0.01358

    D                E
-0.04110          1.25447
```

The SIGMA and K values indicate the quality of the fit. The SIGMA is the standard deviation of the regression and is equal to

$$\text{SIGMA} = \left(\sum \frac{(C_a - C_o)^2}{n-k} \right)^{1/2}$$

where $(C_a\text{-}C_o)^2$ is the square of the deviation between observed (o) and accepted (a) concentration values; n = number of samples and k = (number of regression coefficients + the number of calculated influence coefficients (alphas)). Thus, if no alphas are included, k = 2 for a straight line calibration. The K factor is related to the standard deviation and is inversely proportional to the overall concentration levels in the regression (SIGMA = K C1/2). The regression program is arranged to reduce the K factor to a minimum.

If the k is too large for the number of standards being used in the regression, an appropriate message will be printed out.

The overall quality of fit can be observed by typing:

<u>PRL</u> (= print results list)

The system will indicate the following:

```
INTENSITY,                  (observed)
CHEMICAL CONCENTRATION,     (input manually through ACD)
CALCULATED CONCENTRATION,
CONCENTRATION DIFFERENCE,
CHEMICAL APPARENT CONCENTRATION
```

(Equal to the value C/(1 + SUM aC) from the DJ correction formula. If no alphas are used, the chemical apparent concentration is equal to the chemical concentration),

```
CALCULATED APPARENT CONCENTRATION,
IDENTIFICATION.
```

The operator can introduce alpha corrections using the command

<u>CAL XX</u> (CAL = calculate alpha)

where XX is the element influencing the result.

All alphas can be eliminated using command

<u>RCF</u> (reset)

Samples can be removed from the calibration list using command DSA and restored using ISA.

Plots can be observed on graphic terminal using command PLT.

Once the regression is deemed satisfactory, the D, E and alpha values can be stored at the appropriate <u>Calculation Parameter (CP) Set</u>. The CP set is identified by number (as listed in the LP set). To place the regression parameters in the CP set, the operator enters:

<u>SRR 1</u> (store regression results in CP 1)

If CP1 is a new list, the system responds with

```
NEW LIST
NAME  :        (can enter any name or title desired, e.g. Major  Elements)
NDEC = 3: =    (number of decimal places)
```

If the CP not new, then only the number of decimal places desired is requested.

If the same analyte (and influencing elements) is found in a different CP listing, and if upgrading is also required, the SRR instruction can be repeated, directing the D, E and alpha values to the other CP set. This is very useful in that small groups of elements can be calibrated separately (and more quickly) and new curves be installed in several CP sets.

The instruction PCP allows the operator to view the full calculation parameter set. The instruction ACP (assemble calculation parameters) can be used to enter manually the D, E and alpha values if required.

To regress on another analyte, the operator types

NRE (= next regression element)

```
REGR. ELMNT :
```

To go back to the main program, the operator exits from the regression program (END) and re-enters the X14 software (MCR X14). It is possible on the MICRO11 computer to run the system from the printer and to leave the graphics terminal in the regression routine. It is important to remember however, that the same file cannot be open at both terminals.

There are several re-calibration routines available on the PW1400 software. The operator is referred to the operator's manual.

Scanning

As a sequential instrument, the PW1400 can produce excellent scan results. The graphics terminal can be used effectively to enhance scans of regions of interest and produce usable plots at the dedicated printer.

To obtain a scan with output in both numerical and graphical display, it is important to:

- be sure the system is in automatic mode
- have the sample in the correct measurement position (turret)
- assure the data is stored on disk - this can be done by typing
  WDD XXXXXX (= write data to disk)
  where XXXXXX = name of data file

Since the scan will likely be near an analyte of interest, the operator may want to use the parameters for that element for the scan. Thus, for example, if the scan is in the region corresponding to analyte Cu, the operator enters:

SCH CU

The operator then sets the scanning conditions:

- time for counting at each point:

PTS 1 (1 sec)

- initial (starting) angle:

SLF 45 (slew to 2-theta = 45°)

- final angle and scanning increment:

  STS 50 0.05 (scan to 50° in 0.05° increments)

This final instruction will begin the scan. If the system is in automatic mode with a WDD instruction, the system will write the filename XXXXXX.YYY, which is to contain the scan information. The filename subscript (.YYY) is assigned by the computer. As the scan proceeds, the numerical intensity value at each point will be listed at the printer (terminal) as it is obtained.

If the scan is performed in the manual mode, then the only presentation of the scan consists of the numerical output appearing at the printer. However, if the scan data is stored, then the file can be opened and a plot created.

To open file:

```
OPF XXXXXX.YYY
```

To plot scan:

`PLS` (the terminal should be the graphics terminal)

The system then responds with a series of messages allowing the operator select the mode of presentation (as curve or as points) as well as a choice of start and end angle. The full scale width of the intensity (count) axis is then printed (and either accepted or changed) and the plot put out on the screen. The screen can be "dumped" to the dedicated printer (LA50) for a hard copy output of the plot.

If a series of scans is to be obtained for the same angle range (and under the same conditions), the instructions can be set into a JOB stored in the parameter bank.

For example, to setup a job for a scan from 45 to 50° (increment 0.05°) under the conditions normally used for measuring copper, the following steps are carried out:

`AJB 1` Assemble job # 1

1 EJB: = The first step is assumed to be the end of the job (default). The first instruction is then entered.

```
1 EJB : =  SCH CU
2 EJB : =  PTS 1.0
3 EJB : =  SLF 45.0
4 EJB : =  STS 50.0 0.05
5 EJB : =  [R]
```

To perform the scan, one types:

```
WDD XXXXXX
SJB 1              (Start Job 1)
```

There are many combinations of instructions which can be included in a jobfile (multiple scans, angle calibration, sample measurement). To delete a jobfile from the PB, type:

```
DJB 1
```

Running the Sample

Once the Measurement Program (MP), Link Program (LP), rate correction set (RC), and the Calculation Parameter (CP) sets have been defined, it is possible to run samples on a routine basis.

DETERMINATION OF MAJOR ELEMENTS
(SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO)
FLAME ATOMIC ABSORPTION SPECTROMETRY

Introduction:

These methods are used only where the sample matrix makes the constituents concerned unsuitable to be determined by XRF. This will arise, for example, when the sulphur or iron content of the rock is too high to allow a fused bead to be prepared for XRF determination. This method is also applied when the silica content is between 10 and 30 percent and existing programs for determination by XRF in this range are unsuitable.

Silicon - Silicon is the second most abundant element in the lithosphere after oxygen. The simplest classification of silicate rocks is based upon silica content (SiO_2), which is normally in the range of 35 to 80 percent. Quartzites and sandstones may contain 90 to 95 percent silica. The carbonate rocks are a large and varied group of igneous (carbonatite), sedimentary and metamorphic rocks, with silica content ranging from <1percent (calcite and certain marbles) to 30 percent in some sediments and carbonatites.

Silica occurs in crystalline forms (quartz, tridymite, crystoblite), and in the amorphous state (opal, onyx, chalcedony). More commonly, silica combines with magnesium, iron, aluminium, alkali and alkaline earth elements to form complex silicate minerals. These include rock-forming minerals such as: olivine, pyroxenes, amphiboles, micas, feldspars, feldspathoids (e.g. nepheline, leucite, sodalite), and aluminosilicates (kyanite, kaolin, sillimanite). Other minerals such as zircon, tourmaline, and sphene also contain silica.

Aluminium - Aluminium follows silicon as the third most abundant element in the earth's crust. The concentration of aluminium depends on the magmatic sequence of crystallization. The aluminium content in rocks is typically from 10 to 25 percent. Aluminium content decrease in order (dolerite, basalt, gabbro) > (andesite, diorite)> (tonalite, granodiorite)>(granite, rhyolite).

Some of the more important minerals of aluminium do not crystallize in the main stages of silicate differentiation, but appear with rare element concentration at the pegmatite and other late stages of rock emplacement. These include beryl, spodumene, topaz, and cryolite. Andalusite, sillimanite and kyanite may contain up to 60 percent Al_2O_3. Rarer aluminium minerals include corundum, chrysoberyl, turquoise, alum and alunite. The main sources of aluminium metal are the bauxite and laterite ores which result from weathering, leaving aluminium as an insoluble residue.

Iron - Iron is the fourth most abundant element comprising about 5 percent of the earth's crust. Basic rocks may contain 30 to 40 percent iron (as FeO), while many acidic rocks contain as little as 1 percent total iron. Ferric iron is frequently associated with aluminium, and ferrous iron with magnesium.

Sulphide minerals such as pyrite, pyrrhotite and chalcopyrite are common. Iron carbonate minerals are siderite or chalybite $FeCO_3$ and ankerite which is a mixed carbonate of iron, calcium and magnesium.

Calcium - Calcium ranks fifth in the order of elemental abundance. Rocks which crystallize early, contain small amounts of calcium (periodotites, dunites). Sucessive crystallization forms calcium-rich feldspars. Calcium containing silicate minerals include: augite, hornblende, amphiboles, and the plagioclase feldspars. Final crystallization occurs from a calcium depleted magma, resulting in rocks with less calcium (granite, rhyolite).

Calcium carbonate minerals include calcite and aragonite $CaCO_3$ and dolomite $CaMg(CO_3)_2$. Non-silicate minerals of calcium include the sulphates gypsum $CaSO_4.2H_2O$ and anhydrite $CaSO_4$, fluorite CaF_2, perovskite $CaTiO_3$ and scheelite $CaWO_4$.

Magnesium - Magnesium (seventh in abundance in earth's crust) can constitute as much as 51 percent as MgO in certain silicate rocks (dunite), or 30 to 40 percent in ultrabasic rocks (picrites and peridotites). Magnesium content decreases in the order (dolerite, gabbro, basalt)> andesite> (granodiorite, tonalite)> granite. During crystallization of ferromagnesian minerals, the first solid fractions are enriched in magnesium relative to the composition of the magma, the last fractions are enriched in iron.

Magnesium carbonate minerals include magnesite $MgCO_3$ and dolomite $CaMg(CO_3)_2$.

Manganese - Manganese has an average crustal abundance of 600 ppm. The highest manganese contents occur in the earliest rocks to crystallize (peridotites, basalts and gabbros). Granites and rhyolites contain only very small amounts of manganese. Clays and shales contain manganese in amounts similar to igneous rocks.

Manganese carbonate rocks are variable, ranging from manganese-poor chalk and limestones, to the manganese-rich ankeritic carbonates.

Safety advisory:

1. Exercise extreme care when using any acids and fluxes required for sample dissolution. Their use should only be attempted after the appropriate **MSDS** sheets have been read and the safe handling and first aid procedures understood. Acids should only be handled in a fumehood designated for their use and proper protective equipment worn. Proper ventilation is required when handling fluxes which create a dust control problem.

2. Before operating an atomic absorption spectrophotometer, ensure that the instructions found in the manufacturer's operator's manual are understood.

3. Cylinders of compressed gas used as fuel and oxidant for flame atomic absorption spectrometry must be securely fastened and have the proper regulator. Ensure that the system has no leaks and the gas hoses are in good condition. Review the section on compressed gases found in the Geoscience Laboratories' Safety Manual.

4. When using HF wear glasses and gloves, and be extremely careful. More information on HF is available in the Geoscience Laboratories' Safety Manual.

Apparatus:

- Varian AA 775
- Nalgene ware, 250 ml beakers, 100 ml, 200 ml volumetric flasks, 500 ml graduated cylinders
- Porcelain crucibles (Coors High-Form, 30 ml)
- Graphite crucibles (32x29 mm, 9 ml)
- Magnetic stirrers with teflon stirring bars
- Thermolyne Muffle Furnace
- Silica tray
- Crucible tongs
- Filtering funnels
- Whatman #41 filtering paper, 12.5 cm

Reagents:

- Lithium metaborate, anhydrous, $LiBO_2$
- Hydrofluoric acid, HF, 48%
- Strontium nitrate, $Sr(NO_3)_2$
- Boric acid crystal, H_3BO_3
- Silica powder, SiO_2
- Graphite powder

Method:

The method consists of the following techniques.

1. Samples are fused with lithium metaborate and dissolved using HF

2. Analyte concentrations are measured by atomic absorption spectrometry

3. Calculation of results using calibration curves produced from reference materials

NOTE: For routine work, in-house reference materials are used. In special cases, certified reference materials may be used. These reference solutions may be store in polypropylene bottles and used for a number of sample batches.

Procedures:

1. Reagent preparation

1.1. Hydrofluoric acid (10%) stock solution - Add 125 ml of 48% HF to 375 ml of distilled water in a 500 ml nalgene graduated cylinder. Store in a clean and empty polypropylene supplier container.

1.2. 30,000 ppm Strontium Buffer - Dissolve 72.0 g of strontium nitrate in distilled water and make to 1 liter volume with distilled water. (see Note 1)

2. Sample Decomposition

2.1. Weigh 0.200 g of sample into a porcelain crucible. (see Note 2)

2.2. Add 1.0 g of lithium metaborate and mix sample and flux with a small teflon coated spatula. (see Note 3)

2.3. Transfer quantitatively to a graphite crucible and place on a silica tray. (see Note 4)

2.4. Fuse in a muffle furnace for 15 minutes at 1000°C.

2.5. Open the oven door and pour the fused sample while hot; using crucible tongs and protective gloves, into a 250 ml nalgene beaker containing 60 ml of 10% HF solution.

2.6. Add 4.5 g of boric acid crystal to the beaker and add 100 ml of distilled water.

2.7. Place a teflon-coated stirring bar in the beaker and place on a magnetic stirrer unit. Stir for 30 to 60 minutes, depending on the type of sample, or until dissolution is complete. (see Note 5)

2.8. Filter the solution using Whatman #41 filter paper (12.5 cm) into a 200 ml nalgene volumetric flask. Wash filter paper and beaker several times with small amounts of distilled water. Make to volume with distilled water. This is the original stock sample solution A.

2.9. Prepare solution to be used for the AA determination of CaO, MgO, and Fe_2O_3.

2.9.1. Pipet 10 ml of sample stock solution A into a 100 ml nalgene volumetric flask.

2.9.2. Pipette 5 ml of 30,000 ppm Sr buffer solution to the flask and make to volume with distilled water.

2.10. Prepare solution to be used for the AA determination of SiO_2 and Al_2O_3.

2.10.1. Pipet a 50 ml aliquot of sample stock solution A into a 100 ml nalgene volumetric flask.

2.10.2. Add 10 ml of 30,000 ppm Sr buffer solution to the flask and make to volume with distilled water.

2.11. Retain remainder of stock sample solution A for the determination of MnO.

NOTES:

1. The strontium nitrate should be checked for the presence of major elements as contaminants, in particular for calcium. In addition, a reagent blank should be prepared with each batch of samples.
2. If the samples are high in sulphur or organic material, weighed samples placed in a porcelain crucible should be roasted in a muffle furnace at 650°C for three to four hours, or preferably overnight.
3. For samples known to contain >30% iron oxide, add about 15 mg of pure graphite powder to the porcelain crucible containing sample and flux. This will aid when pouring the fused melt and prevent it from sticking to the bottom of the graphite crucible.
4. New graphite crucibles need to be conditioned by placing in a muffle furnace at 1000°C for 15 minutes.
5. It is important that after fusion, the samples should be stirred until dissolved, filtered and made to volume (200 ml) on the same day to ensure a faster dissolution of calcium and magnesium fluorides and prevent precipitation of silica.

3. Calibration and measurement of analyte

The atomic absorption spectrometer is calibrated with in-house and certified reference materials prepared as solutions in the same manner as that used for samples. Manganese content of geological materials is usually less than 2000 ppm. If the manganese is to be reported as ppm its determination can be made using pure aqueous standards containing manganese for calibration (see Traces - AA, page EA17-1). Table MAAS1 (page EA7-4) serves as a guide for chosing which certified or in-house reference materials to use. Once prepared, these solutions may be stored in polypropylene bottles and used for calibration at a later date.

NOTE: CRM are valuable and should only be used in research work or for programs for certification. In-house MRB reference materials should be utilized for routine work.

To calibrate samples which contain greater than 75% SiO_2, silica standards can be prepared using 0.200g pure silica powder to obtain a stock solution of 1000 ppm SiO_2. Prepare a solution as in procedure 2.10 to give a calibration standard equivalent to 100% SiO_2. Smaller volumes of stock solution will produce calibration standards less than 100%, i.e., 45 ml will yield a 90% SiO_2 calibration standard. Check the silica standards against a few reference materials to ensure consistent results for silica.

TABLE MAAS1. CONCENTRATION OF CERTIFIED REFERENCE MATERIALS
To be used for Calibration when Determining
Major Elements by AAS

CRM	% SiO_2	% Al_2O_3	% CaO	% MgO	% Fe_2O_3
GA	69.8	14.5	2.45	0.95	2.86
GH	75.8	12.5	0.65	0.03	1.33
BR	38.5	10.2	13.74	13.28	12.92
DTS	40.6	0.29	0.14	49.75	8.59
Mica-Fe	34.4	19.6	0.45	4.65	25.76
SY-2	60.07	12.15	8.03	2.66	6.33
SY-3	59.7	11.7	8.30	2.63	6.45
MRG-1	39.22	8.51	14.68	13.49	17.9
NBS-1a	14.1	4.16	41.32	2.19	1.63
NBS-88a	1.20	0.19	30.1	21.3	0.28
PCC-1	41.9	0.73	0.53	43.37	8.23

Other CRM's can be substituted for those listed above. A complete list of CRM available in the laboratory can be obtained from the Geostandards Coordinator.

A Varian AA775 is used for the determination of major elements in fluoborate solutions. See "Operation of the Atomic Absorption Spectrophotometer - Varian AA775" on page EA4-1 for details.

Consult the element specific information sheets for the necessary details to perform the determination of each major element. Titanium, chromium and barium are possible additional elements which can be determined using **sample stock solution A**. Sensitivity limitations may restrict the usefulness of the range of concentration for these elements. Trace elements in rocks are generally not sufficiently concentrated in the fluoborate solution for determination by flame AAS.

4. Calculation and reporting of results

After calibration, all readings are in percent oxide of the element. Readings are recorded, blank corrected and multiplied by the appropriate dilution factor.

Major 1 and Major 2 Analysis Worksheet forms are to be used for reporting analytical results. Results are reported as Percent Oxide (% Oxide). Three significant figures are reported in the range 99.9% to 1.00%; two significant figures for 0.99% to 0.01%.

Less than 0.01% is indicated by 0.00%. A blank means that the element was not determined. N.D. (none detected) or <(less than) are not allowed.

Quality control:

The determination limits and precision for individually determined "major components" by AAS are listed below.

TABLE MAAS2.

Oxide	Determination Limit (Percent)	Precision* at MRV (Abs.Percent)	MRV (Percent)
SiO_2	1.0	1.0	30
Al_2O_3	0.2	0.4	10
Fe_2O_3	0.2	0.4	5
CaO	0.1	0.4	3
MgO	0.1	0.4	3

*Precision is the 95% confidence limit (2σ). For example CaO at the 3 percent level is determined to ±0.4 percent (absolute).

MRV Mid-range value.

Silicon Dioxide **SiO_2**

STANDARD SOLUTIONS

Use certified reference materials and pure silica powder prepared in the same manner as the samples.

INSTRUMENT PARAMETERS

Lamp Current (ma)	10
Wavelength (nm)	251.6
Spectral Band Pass (nm)	0.2

Flame Description
Nitrous oxide-acetylene
Fuel rich, red cone 10-15 mm high

INTERFERENCES

NOTES

1. The burner height position is very important as there is a very narrow region of the flame where Si absorbs.
2. If single beam mode is used allow 30 minutes for lamp warm-up.
3. Scan samples for concentration range in order to bracket the sample with standards. This is necessary as only a few samples can be run before burner blockage becomes excessive.
4. Before turning flame off, reduce the fuel control down on the instrument, particularly if fuel flow is greater than 100.

Aluminium Oxide **Al_2O_3**

STANDARD SOLUTIONS

Use certified reference materials prepared in the same manner as the samples.

INSTRUMENT PARAMETERS

Lamp Current (ma)	10
Wavelength (nm)	309.3
Spectral Band Pass (nm)	0.5

Flame Description
Nitrous oxide-acetylene
Fuel rich, reducing, red cone.

INTERFERENCES

Aluminium is partially ionized in a nitrous oxide-acetylene flame. The added strontium acts as an ionization buffer.

Interferences are dependent on flame conditions and burner height. A fuel rich flame (red cone) decreases the effect.

Silicon depresses aluminium absorbance by the formation of an undissociated refractory complex. This is minimized by the addition of Sr as well as matching standards and samples with respect to the major matrix elements.

NOTES

1. Fuel-support ratio and burner height are critical in the determination at low levels of detection.
2. Burner blockage, although not as severe as with silica, will occur with fuel rich flames. Bracket samples and standards when reading absorbances.

Calcium Oxide CaO

STANDARD SOLUTIONS

Use certified reference materials prepared in the same manner as the samples.

INSTRUMENT PARAMETERS

Lamp Current (ma)	3.5
Wavelength (nm)	422.7
Spectral Band Pass (nm)	0.5

Flame Description
Air-acetylene
Oxidizing, fuel lean, blue

INTERFERENCES

Silicon, aluminium, phosphate and sulphate depress the calcium absorbance. These interferences can be controlled by introducing a releasing agent such as strontium and by matching sample and standard solutions to obviate combined interference effects.

The slight ionization interference which occurs with the air-acetylene flame, is controlled with the added strontium.

A nitrous oxide-acetylene flame causes severe ionization of calcium. The addition of a readily ionizable substance will overcome this effect.

NOTES

1. The depression of calcium signals (air-acetylene flame) is caused by elements which give rise to stable oxysalts.
2. The presense of a cyanogen emission band at 421.5 nm may cause an increase in background noise if not completely separated by the monochromator.
3. The formation of oxysalts is virtually eliminated with the use of a nitrous oxide-acetylene flame. To control the resulting ionization of calcium with this flame, 0.2% potassium salt should be added to both samples and standards.
4. Noise level was observed to be excessive when the nitrous oxide-acetylene flame was used and the air-acetylene flame is preferred.

MagnesiumOxide MgO

STANDARD SOLUTIONS

Use certified reference materials prepared in the same manner as the samples.

INSTRUMENT PARAMETERS

Lamp Current (ma)	3.5
Wavelength (nm)	285.2
Spectral Band Pass (nm)	0.5

Flame Description
Nitrous oxide-acetylene
Fuel lean
Air-acetylene
Oxidizing, fuel lean, blue

INTERFERENCES

Interferences are similar to those which occur with calcium, i.e., silicon, aluminium, phosphate and sulphate will depress the magnesium signal in the air-acetylene flame. Strontium addition and matrix matching of samples and standards will correct for these interferences and any ionization of magnesium in the flame.

Ionization of magnesium in the nitrous oxide-acetylene flame is controlled with the added strontium to the solutions.

NOTES

1. Nitrous oxide-acetylene flame is preferred, although the air-acetylene flame could be used in the same manner as with the determination of calcium.
2. The signal noise with the nitrous oxide-acetylene flame is not as severe as that observed when determining calcium with this flame.
3. The fluorborate solutions tend to diminish the chemical interferences in the flame attributed to the formation of "inter-oxide" compounds such as magnesium aluminate, calcium silicate, etc. A fluorborate solution binds interfering elements to fluorine, whereas sulphate and phosphate interferences would probably not be eliminated.

Iron Oxide (Total Iron) Fe_2O_3

STANDARD SOLUTIONS

Use certified reference materials prepared in the same manner as the samples.

INSTRUMENT PARAMETERS

Lamp Current (ma)	5.0
Wavelength (nm)	248.3
Spectral Band Pass (nm)	0.2

Flame Description
  Air-acetylene
  Oxidizing, fuel rich, blue

INTERFERENCES

Matrix matching of samples and standards is recommended.

DETERMINATION OF MAJOR ELEMENTS (SiO_2, Al_2O_3, CaO & MgO) CLASSICAL (GRAVIMETRIC) METHOD

Introduction:

For an introduction about the abundance and occurrence of the major elements, refer to, 'Determination of Major Elements by Flame Atomic Absorption Spectometry', page EA7-1 of this manual.

Although largely superceded by more productive instrumental methods, classical methods for the determination of major elements have generally not been surpassed in terms of the quality of data produced.

The Geoscience Laboratories participates in projects with national and international laboratories and uses these methods for certification purposes.

These method are also used where the sample matrix makes the constituent concerned unsuitable to be determined by XRF. This will arise when the sulphur content of the rock is too high to allow a fused bead to be prepared by XRF.

Safety advisory:

1. When using HF wear glasses and gloves, and be extremely careful. More information on HF is available in the Geoscience Laboratories' Safety Manual page IV-17.

2. Other acids are used throughout this method, and all staff must review the appropriate MSDS sheets.

Apparatus:

- Platinum crucibles, 25 ml with covers
- Glazed porcelain casseroles, 250 ml
- Watch glasses, 12 cm, supported by glass triangles
- Glass rods
- Platinum tipped tongs
- Glass beakers, 250 ml, 400 ml, 600 ml, 800 ml and 1000 ml
- Glass funnel, 75 mm
- Filter papers, 12.5 cm Whatman No. 40, 41, and 42
- Bunsen burner
- Meker burner
- Muffle furnace
- Hot plate
- Thermofab cloth
- Silica tray
- Graphite crucibles (32 X 29 mm, 9 ml)
- Teflon coated stirring bars
- Magnetic stirrers
- Nalgeneware, 100 ml and 200 ml volumetric flasks, 250 ml beakers, and 100 ml graduated cylinder

Reagents:

- Sodium carbonate, anhydrous, Na_2CO_3
- Lithium Metaborate, anhydrous, $LiBO_2$
- Boric acid crystals, H_3BO_3
- Concentrated hydrochloric acid,HCl, 36.5% - 38%
- Concentrated nitric acid, HNO_3, 69.0% - 71.0%
- Concentrated hydrofluoric acid, HF, 48%
- Concentrated sulphuric acid, H_2SO_4, 96%
- Strontium nitrate, $Sr(NO_3)_2$
- Ammonium hydroxide, HN_4OH, 28% - 30%
- Ammonium oxalate crystals, $(NH_4)_2C_2O_4.H_2O$
- Ammonium chloride crystals, NH_4Cl
- Diammonium phosphate crystals, $(NH_4)_2HPO_4$
- Ammonium nitrate, $NH_4.NO_3$

Method:

The method consists of the following techniques:

1. Fusion and decomposition of the sample by acid digestion

2. Precipitation of SiO_2, R_2O_3, CaO and MgO

3. Separation of SiO_2, R_2O_3, CaO and MgO

4. Weighing of SiO_2, R_2O_3, CaO and MgO

5. Calculation of results

NOTE: R represents a group of elements - Al, Fe, Ti, and P - which are precipitated as the hydrated oxide by means of ammonium hydroxide in the presence of ammonium chloride. Ammonium chloride is added to prevent the precipitation of $Mg(OH)_2$.

Procedures:

1. Reagent preparation

1.1. 6% ammonium oxalate solution $(NH4)_2C_2O_4.H_2O$ - Heat solution to dissolve, filter and make solution to volume with distilled water.

1.2. 20% Diammonium phosphate solution $(NH_4)_2HPO_4$ - Dissolve in distilled water, filter and make to volume with distilled water.

1.3. 2% Ammonium nitrate solution - Dissolve in distilled water, neutralize with ammonium hydroxide using a methyl red as an indicator, and filter.

1.4. 0.1% Ammonium oxalate solution - Dissolve in distilled water, if necessary by heating, and filter.

1.5. 5.0% Ammonium hydroxide solution v/v in distilled water.

1.6. 5% Hydrochloric acid solution v/v in distilled water.

NOTE: Make solutions in quantities sufficient for the number of samples to be analyzed.

2. Fusion and sample decomposition

2.1. Weigh exactly 0.800 g of sample in a clean 25 ml platinum crucible. Weigh 4 g (on top loading balance) of Na_2CO_3 flux. Mix with a small teflon rod.

NOTE: If sample is very high in sulphides or ferrous iron, a gentle preliminary roasting, in the crucible, of the weighed, unmixed sample at a dull red heat for several minutes is desirable to prevent any subsequent reduction of FeO to metallic iron, which then alloys with the platinum. By fusing with a basic flux the minerals of the rock are changed into compounds which are soluble in HCl.

2.2. Return the covered crucible to the triangle support and heat the crucible with a low flame for approximately 5 - 10 minutes over a Meker burner. Then use full heat for 20 - 30 minutes. At no time should the flame envelop the crucible, nor should the crucible bottom ever come into contact with the blue cone of the burner flame.

2.3. Heat the outer surface of the lid with another burner to fuse any particles that may have been spattered on the inner surface of the lid. It is good practice to move back the lid, grasp the crucible firmly with platinum tipped tongs and swirl it to incorporate any unfused material clinging to the sides of the crucible.

2.4. Remove the crucible cover and carefully place it, face up, on a clean watch glass. Grasp the crucible with platinum tipped tongs, remove it from the flame and rotate the crucible as it cools, so that the contents solidify around its walls.

2.5. Cool on a marble slab. Re-heat the crucible with the Meker burner until the inside becomes red but does not melt. Cool as before.

NOTE: The second heating helps break away the cake from the crucible.

2.6. Using a wash bottle, direct a jet of distilled water around the top edge of the cake. This will usually undermine and loosen it.

2.7. Place the crucible lid in a 250 ml glazed porcelain casserole and cover with water. Add a few drops of HCl and heat till all adhering particles are dissolved.

2.8. Remove the lid using platinum tipped tongs and a glass rod, and rinse into the casserole. Carefully transfer the platinum crucible with the cake after wiping the bottom of the crucible with wet tissue. Tilt the crucible on one side, with the glass rod and add approximately 75 ml of distilled water.

2.9. Cover the casserole with a watch glass supported by glass triangle and carefully add 20 - 25 ml of concentrated HCl from a graduated cylinder. Set the covered casserole on hot plate.

2.10. Heat on "medium" setting and gently press the cake with glass rod until the cake loosens and disintegrates. At this stage, if any unattacked gritty residue is noticed probing with the glass stirring rod, the sample should be discarded and the fusion repeated at a higher temperature.

2.11. Remove the platinum crucible using platinum tipped tongs.

2.12. Police (using a rubber policeman) the inside and outside of the crucible to remove adhering particles, adding all rinses to the casserole.

2.13. Rinse the policeman and glass rod into the casserole.

2.14. Set the casserole, with watch glass supported by glass triangle, on a hot plate covered with thermofab cloth. Set the temperature of hot plate between low and medium and evaporate to dryness.

NOTE: On adding HCl to the mixture, chlorides of all metals present are formed, carbonates are decomposed, and silicic acid is formed. When a large amount of the latter is present, some of it will precipitate out as white solid. On evaporating the contents of the dish to dryness, the silicic acid present is partially dehydrated, and becomes almost insoluble in dilute HCl.

NOTE: Thermofab cloth on the hot plate and moderate temperature prevents splattering of the residue of silicic acid and other salts at the final stage of drying.

3. Determination of SiO_2

3.1. Silica - first filtration

3.1.1. To the cool residue add 5 ml of concentrated HCl, wetting all of the residue and particularly the ring marking the original level of the liquid in the casserole, from which it is difficult to remove particles of silica.

NOTE: If distilled water is added first, insoluble basic salts of iron are apt to form, especially if the residue is warm.

NOTE: The first filtrate from the silica still contains a small amount of silicic acid, which requires a second evaporation for recovery. This usually amounts to 10 mg SiO_2.

3.1.2. Allow to stand 1-2 minutes and then add approximately 50 ml of distilled water, washing down the sides of the casserole and the stirring rod.

3.1.3. Cover and carefully heat the casserole on the hot plate until all soluble salts have dissolved as indicated by an absence of gritty particles. This heating should not be prolonged in order that as little as possible of the silica will be dissolved and more water may be added if necessary in order to make fast dissolution of the salts.

3.1.4. Remove from the hot plate and filter into a 250 ml beaker using a 12.5 cm Whatman No. 41 filter paper.

3.1.5. Use a policeman to remove adhering silica.

3.1.6. Finally, wash the residue and filter paper 10 times with the hot 5% HCl solution. Cover the funnel with ordinary filter paper and reserve.

3.1.7. Quantitatively transfer the contents of the beaker to the original casserole and evaporate the contents to dryness as before.

3.2. Silica - second filtration

3.2.1. Add 5 ml concentrated HCl to the cool residue, wetting all of the residue.

3.2.2. Allow it to stand 1-2 minutes and then add approximately 50 ml distilled water. Heat the casserole on the hot plate carefully until all soluble salts have dissolved.

3.2.3. Filter without delay using a 12.5 cm Whatman No. 40 filter paper in a 72 mm funnel as described previously, catching the filtrate in a 400 ml beaker.

3.2.4. Thoroughly police the inside of the casserole and the stirring rod, and add all washings to the filter funnel.

3.2.5. Wipe the stirring rod and lip of the casserole with a piece of filter paper and add it to the funnel.

3.2.6. Finally, wash the paper and the residue 10 times with hot 5% HCl solution, paying particular attention to the upper edge of the paper. Lift the paper to drain the stem of the funnel and rinse the tip of the funnel into the beaker.

3.2.7. Cover the beaker and reserve the filtrate for other determinations.

NOTE: A small amount of silica still escapes recovery and goes into the filtrate from the second evaporation and filtration. This is recovered from the R_2O_3 precipitate and determined by AA after fusing with $LiBO_2$ in a platinum crucible.

3.3. Silica - ignition of precipitate

3.3.1. Carefully fold the papers in the funnels with platinum tipped forceps and transfer them to the original platinum crucible.

3.3.2. Wipe out the insides of the funnels with a piece of filter paper and add it to the crucible.

3.3.3. Place the crucible with the cover not quite in place, using a clean fused-silica small tray, in a cold electric muffle furnace and burn off the paper by allowing the temperature to rise slowly.

3.3.4. Ignite the residue at 1000°C for 30 minutes (the full heat of a Meker burner may be used but the furnace is preferred.)

3.3.5. Cool the covered crucible in a desiccator for 30 minutes and weigh it.

3.3.6. Return the covered crucible to the muffle furnace for 20 minutes, cool for 30 minutes in a desiccator and again weigh it.

3.3.7. Continue to ignite for 20 minutes periods until two subsequent weights differ by no more than 0.0002 g. The final weight is that of the impure silica.

3.4. Silica - Treatment with HF to determine impurities

3.4.1. Cautiously moisten the residue with approximately 1 ml of distilled water and add 6 drops of dilute H_2SO_4 (1:1).

3.4.2. Quickly pour 10 ml of HF (48%) into the crucible and replace the cover.

3.4.3. Allow the crucible to stand for 1 or 2 minutes to permit the initial reaction to take place, then place the covered crucible on a hot plate, covered with a thermofab cloth, at about medium temperature in a fume hood and allow to stand covered for 5 minutes.

NOTE: The ignited silica residue is never pure, but always contains small amounts of Fe, Al and Ti oxides. If the washings were careless it may also contain NaCl. Silica from rocks high in Fe and Ti is usually the most impure.

3.4.4. Remove the cover with platinum tipped tongs (allowing any condensate on the inner surface to drop into the crucible) and cautiously heat the outer surface of the cover with a low flame to volatilize condensed HF.

3.4.5. Evaporate the contents of the crucible to fumes of SO_3 (raise the temperature of the hot plate as needed), then cautiously evaporate the excess H_2SO_4 over a low flame, holding the open crucible with platinum tipped tongs.

NOTE: Care is necessary to prevent spattering, particularly if there is much TiO_2 and Zr present.

3.4.6. When the evolution of SO_3 fumes has ceased, heat the crucible to dull redness to decompose the sulphates that are present.

3.4.7. Cool the crucible and gently wipe the outer surface with a damp cloth to remove adhering sand particles.

3.4.8. Ignite the covered crucible in an electric furnace at about 800°C for 5 minutes, cool and weigh. The difference in weight is that of the pure silica.

3.5. Recovery of SiO_2 from R_2O_3 precipitate and determination by Flame Atomic Absorption

Silica - decomposition

3.5.1. Add 1.0 g $LiBO_2$ to the platinum crucible already having ignited R_2O_3 precipitate, mix well with a small spatula, and cover.

3.5.2. Fuse in a muffle furnace for 15 minutes at 1000°C.

3.5.3. Place on a clean small silica tray.

3.5.4. Open the oven door and remove the crucible using platinum-tipped tongs and place on another clean fused silica tray and cool it.

3.5.5. Place crucibles in a clean 250 ml nalgene beaker.

3.5.6. Place a small teflon coated stirring bar in the crucible.

3.5.7. Add 60 ml of 10% HF.

3.5.8. Add 100 ml of 4.5% boric acid solution.

3.5.9. Stir for 1 hour or more until dissolution is complete.

3.5.10. Filter the solution using Whatman No. 41 filter paper (12.5 cm) into a 200 ml nalgene volumetric flask.

NOTE: If iron is very high, it is difficult to obtain a clear solution. SiO_2 will be attacked and will be in solution.

3.5.11. Wash filter paper and beaker several times with small portions of distilled water. Make to volume with distilled water. This is your original solution.

3.5.12. Pipet 50 ml of original solution to a 100 ml nalgene volumetric flask.

3.5.13. Add 10 ml of 30,000 ppm Sr buffer solution to the flask and make to volume with distilled water.

3.5.14. Determine SiO_2 as described in the method Major Element Determinations by Flame Atomic Absorption, page XXX.

3.5.15. Add this SiO_2 value to the value of pure SiO_2 to obtain total SiO_2.

4. Determination of R_2O_3 (All Fe, Al, Ti and P)

4.1. R_2O_3 precipitation

4.1.1. The filtrate from the second silica filtration is used which should be in a 400 ml beaker.

NOTE: All of the iron present in this filtrate is in the ferric form, due to oxidation during fusions and evaporation.

4.1.2. Add 5-6 g of NH_4Cl, depending on the amount of Mg likely to be present, and dilute the solution to 200 ml.

NOTE: NH_4Cl is added to prevent precipitation of $Mg(OH)_2$ with the Fe and Al. The more Mg present the greater the amount of NH_4Cl needed.

4.1.3. Most of the free acid is neutralized by adding pure NH_4OH from a small beaker. If the solution is dark-coloured, indicating the presence of much iron, there is no point in adding a pH indicator, if the solution is light-coloured, add 3 drops of 0.2% methyl red (60% alcoholic solution, pH 4.2 - 6.3).

4.1.4. Heat to boiling, reduce the heat, and then add pure aqueous ammonia from a dropping bottle until a permanent precipitate forms, stirring vigorously at all times.

4.1.5. The precipitate will appear textureless until near the end point, at which stage it will coagulate. If an indicator was used, the supernatant liquid will be yellow at the end point.

4.1.6. If an indicator was not used, the nearness of approach to the end point can be tested for by adding a drop of the indicator to the quiescent solution and noting the colour of the drop as it strikes the surface.

4.1.7. Allow the precipitate to settle and confirm that the end point has been reached; the solution should smell faintly of ammonia.

4.1.8. Boil for one minute, let precipitate settle and filter through a well fitted 12.5 cm Whatman No. 40 filter paper, in a 75 mm filter funnel.

NOTE: An excess of ammonia is avoided to prevent the redissolving of $Al(OH)_3$. An excess has no effect on $Fe(OH)_3$ or $Ti(OH)_4$.

4.1.9. Catch the first few milliliters of filtrate in a 150 ml beaker. If the filtrate is cloudy, re-filter, catching the solution in the original beaker. Repeat these steps until a clear filtrate is obtained.

NOTE: In this ammonia precipitation Fe, Al and Ti present are precipitated as hydroxides. Any small amount of phosphate present is also precipitated as Fe or Al phosphate.

4.1.10. When the filtrate is clear, replace the small beaker with one of 600 ml capacity and filter the remainder of the solution as readily as possible, keeping the bulk of the precipitate in the beaker.

NOTE: The filtrate from this precipitate contains ammonia and sodium salts, as well as Ca, Mg and most of the Mn orginally present.

4.1.11. Transfer the precipitate to the paper, wash the beaker and stirring rod twice with hot 2% NH_4NO_3 (neutralized) solution. Wash the paper and precipitate ten times, taking care to wash the precipitae away from the edges of the paper.

4.1.12. Wipe the lip of the beaker and the stirring rod with a small piece of filter paper and add this to the funnel.

NOTE: It is difficult to wash this precipitate thoroughly, due to its gelatinous nature. By re-dissolving in acid and re-precipitating, a much better separation is effected.

4.2. R_2O_3 re-precipitation

4.2.1. With the aid of platinum tipped forceps, remove the paper from the funnel and carefully spread it out on the inside wall of the original beaker.

4.2.2. Wash the precipitate from the paper with a jet of hot 5% HCl and rinse the walls of the beaker and stirring rod also.

4.2.3. Place the beaker under the funnel and rinse the funnel with 5% HCl, then with distilled water.

4.2.4. Finally, wash the paper once or twice with distilled water, fold the paper into a triangle with forceps, and drape it over the rim of the beaker.

4.2.5. Heat the contents of the beaker until the precipitate has dissolved (add more 12M HCl if required).

4.2.6. Dilute to about 150 ml and heat to boiling.

4.2.7. Repeat the precipitation as previously described but, when the end point has been reached, add 2 to 3 drops ammonia in excess, and add the filter paper to the solution, shredding it with the stirring rod and forceps and stirring vigorously to macerate it thoroughly.

NOTE: The added pulp from the macerated paper aids in the filtration to follow. Furthermore, when the hydroxide precipitate is ignited, the presence of the paper gives the ignited oxide a porous texture which aids in oxidation of iron to Fe_2O_3.

NOTE: It may be necessary, if there was much acid retained by the paper, to add a few drops of aqueous ammonia to the solution.

4.2.8. Rinse down the sides of the beaker, and heat to boiling for 1 min. Allow the precipitate to settle and filter as before, combining the two filtrates in the 600 ml beaker.

4.2.9. Carefully police the beaker and stirring rod, using the NH_4NO_3 wash solution, and wash the paper and precipitate, 6-8 times with hot 2% NH_4NO_3 wash solution.

4.2.10. Wipe the lip of the beaker and stirring rod with a small piece of filter paper.

4.2.11. Cover funnel with filter paper and set aside until ready to ignite.

4.2.12. Reserve filtrate for determination of Ca and Mg.

4.3. Ignition of R_2O_3 precipitate

4.3.1. With the platinum-tipped forceps carefully lift the paper containing the bulk of the R_2O_3 precipitate from the funnel and place it in the platinum crucible used for the determination of silica.

4.3.2. Fold the upper edges of the paper over the precipitate; avoid soiling the sides of the crucible because, after ignition, it is difficult to remove these stains during the pyrosulphate fusion.

NOTE: As stated above, the residue from the silica consists of Fe, Al and Ti oxides. These belong to the ammonia precipitate, and therefore the later is ignited in the crucible with the silica impurities.

4.3.3. Wipe the upper edge of the funnel with a small piece of filter paper and add it to the crucible also.

4.3.4. The bulky precipitate should be partly dried, or at least well drained, before being placed in the crucible; if not, there is danger that entrained liquid will boil and some precipitate will be lost by spurting.

4.3.5. Partly cover the crucible and place it in a cold electric muffle furnace.

4.3.6. Allow the temperature to rise slowly and ensure that there is free access of air to the furnace during the initial stages of the ignition.

4.3.7. Finally heat at just below 1200°C for 40 minutes, cover the crucible, cool and weigh as usual. When much iron is present it is a useful precaution to transfer the crucible from the muffle furnace to the full heat of a Meker burner for 5 minutes, with the lid displaced to allow free access of air to the crucible, to ensure that oxidation of iron is complete; there is little likelihood of the ignited Al_2O_3 absorbing water having been heated at 1200°C.

4.3.8. Repeat ignition for 20 minutes until constant weight is obtained.

4.3.9. From the total percent of the R_2O_3 oxides, the precentage of Al_2O_3 is obtained by subtracting the percentage of the other constituents of the group, in particular those for total iron (as Fe_2O_3), P_2O_5, TiO_2 and residual SiO_2.

NOTE: Because of number of subtractions from the R_2O_3 precipitate due to presence of Fe_2O_3, TiO_2, P_2O_5, residue SiO_2 and other impurities, the Al_2O_3 value will not be suitable for accurate work. Therefore, Al_2O_3 should be determined by Flame Atomic Absorption as described in the method 'Major Elements by Flame Atomic Absorption Spectrometry', page EA7-1 of this manual.

5.1. Determination of CaO

5.1.1. The calcium is determined in the filtrate from the R_2O_3 precipitate.

5.1.2. Heat the solution in 600 ml beaker and evaporate to about 200 ml. Make it acidic with 12 M HCl.

5.1.3. Add a few drops of methyl orange (0.02% aqueous solution) indicator.

5.1.4. Dissolve 3g ammonium oxalate $(NH_4)_2C_2O_4.H_2O$ in 50 ml of distilled water, heat to 70-80°C and filter through a 12.5 cm Whatman No. 40 paper into the sample solution (if several precipitations are to be done use 50 ml aliquots of hot, filtered 6% solution of ammonium oxalate.

NOTE: The amount of ammonium oxalate to take depends on the amount of Ca to be expected from the nature of the rock, e.g., 3 g ammonium oxalate is enough up to 50% CaO based on a 0.8 g sample weight.

NOTE: The ammonium oxalate solution is filtered to remove small amounts of impurities. Calcium oxalate is often present.

5.2. Calcium - first precipitation

5.2.1. Heat the solution to near the boiling point and add aqueous ammonia (1:1) dropwise, while stirring vigorously, until the indicator changes colour and then add about 1 to 2 ml in excess.

5.2.2. Heat to near boiling (but do not boil) and allow to stand without further heating 2-3 hours with occasional stirring.

5.2.3. When <1% calcium is present the precipitate may not appear for several minutes and calcium should not be judged to be absent until the solution has stood for the time recommended.

NOTE: The calcium oxalate precipitated is never pure but contains occluded magnesium oxalate as well as sodium salts. Hence, after filtering the precipitate is dissolved, re-precipitated and re-filtered.

NOTE: Be careful when heating to avoid bumping, especially where there is a heavy precipitate of calcium oxalate.

5.2.4. Filter the solution through 12.5 cm Whatman No. 40 paper into an 800 ml beaker, retaining as much of the precipitate in the original beaker as is possible. Wash the precipitate 3 or 4 times, by decantation, with cold 0.1% ammonium oxalate and pour the washings through the paper.

NOTE: Due to the common-ion effect, $Ca_2C_2O_4$ is less soluble in weak ammounium oxalate solution than in pure water.

5.2.5. Wash the paper 3 or 4 times with the ammonium oxalate solution. Reserve the filtrate.

5.3. Calcium - re-precipitation

5.3.1. Wash down the sides of the original beaker with hot 5% HCl, add 2 ml 12 M HCl to the solution and heat to boiling to dissolve the precipitate.

5.3.2. Pour the hot solution through the paper, catching the filtrate in a 250 ml beaker.

5.3.3. Wash the beaker thoroughly with hot 5% HCl, pouring all washings through the paper, and then wash the paper thoroughly with the HCl solution, making sure that all areas of the paper are reached (lift up the inside flap with platinum tipped tongs and wash the area beneath it).

5.3.4. Finally, wash the beaker and paper once with water. The final volume should be about 100 to 150 ml.

5.3.5. Remove and discard the paper and rinse the funnel into the solution once with water.

5.3.6. Add approximately 0.5 g ammonium oxalate, dissolved in a few ml of distilled water, to the acid solution; add 2 drops of indicator (methyl orange, 0.02% aqueous solution) and heat the solution nearly to boiling.

5.3.7. Precipitate the calcium as described previously and allow to stand for at least 4 hours, or overnight.

5.3.8. Filter through 12.5 cm Whatman No. 40 paper, combining the filtrate with that obtained from the first filtration, and transferring the precipitate quantitatively to the paper.

5.3.9. Wash the precipitate and paper 10 times with the cold 0.1% ammonium oxalate solution. Reserve the combined filtrates for the subsequent separation and determination of magnesium.

5.4. Calcium - Ignition of calcium oxalate

5.4.1. Place the loosely filter paper in a weighed 25 ml platinum crucible.

5.4.2. Wipe the inside of funnel near top with a small scrap of ashless paper to remove the small amount of precipitate which usually creep up from the edge of paper.

5.4.3. Add it to the crucible, partly cover it.

5.4.4. Burn off the paper at a low temperature in an electric muffle furnace, starting with a cold furnace.

5.4.5. Heat the crucible at 1000°C for 30 minutes (displace the cover slightly at the start to facilitate the escape of carbon dioxide and then cover it tightly), then cool for 30 minutes in a desiccator and weigh rapidly.

5.4.6. Re-heat at 1000°C for 15 minutes, cool for 30 minutes and weigh as rapidly as possible (place proper weights on the balance in advance of the crucible).

5.4.7. Continue heating until constant weight is obtained.

NOTE: When calcium oxalate is ignited it looses CO and CO_2, leaving a residue of CaO, which is weighed. The oxide should be white in colour but occasionally may be light brown or green because of manganese. If the successive separations have been made as described neither of these should be present at this juncture. If a correction for manganese is considered necessary the determination may be made by AA on the solution of the ignited oxide. A knowledge of the strontium and barium content of the sample will indicate whether or not a correction must be applied to the ignited residue for the presence of these elements.

6.1. Determination of MgO

6.1.1. The magnesium determination is made on the filtrate from the calcium filtrations which should be about 400 to 500 ml in a 800 ml beaker.

6.1.2. To the cold (about 10°C) combined filtrates add a filtered solution of dibasic ammonium phosphate $(NH_4)_2HPO_4$ to give approximately 1 g of the reagent per 100 ml of filtrate with 1 g in excess.

6.1.3. Stir and add with vigorous stirring sufficient concentrated aqueous ammonia to make the solution 10% by volume in aqueous ammonia and continue to stir until precipitation begins.

6.1.4. Allow to stand overnight in a fume hood.

NOTE: When any soluble ortho-phosphate salt is added to an ammoniacal solution containing Mg and ammonium salts, the Mg is precipitated as white, crystalline $MgNH_4PO_4$. When this compound is precipitated the first time, from the calcium filtrate it is usually impure due to the presence of large amounts of ammonium and sodium salts in the solution. This is rectified by dissolving the precipitate and re-precipitating under better conditions.

NOTE: Avoid striking the walls of the beaker with the stirring rod during stirring. The abrasion of the glass surface encourages the growth of fine crystals of the precipitate on the walls of the beaker. When only a small amount of Mg is present, however, precipitation can sometimes be initiated in this fashion.

6.1.5. Filter the solution through 12.5 cm Whatman No. 42 filter paper into a 1000 ml beaker, preferably in front of a fume hood. The bulk of the precipitate should be kept in the beaker.

6.1.6. Wash the beaker and precipitate twice with 5% aqueous ammonia (v/v) and pour the washings through the filter; wash the precipitate and paper five times with this wash solution, adding all washings to the filtrate. Reserve the filtrate for subsequent examination.

6.2. Magnesium - re-precipitation

6.2.1. Dissolve the precipitate in the beaker in the minimum volume of hot 5% HCl and rinse down the walls of the beaker.

6.2.2. Cover and heat to near the boiling point and pour the contents of the beaker through the filter, catching the filtrate in a 250 ml beaker.

6.2.3. Wash the paper and funnel with a small amount of hot 5% HCl (raise the inside flap of the paper and wash behind it to dissolve any trapped precipitate) then with water, and remove and discard the paper.

6.2.4. Wash the inside of the funnel once with 5% HCl and then with distilled water; rinse the tip of the funnel into the solution also.

6.2.5. To the filtrate, in a 250 ml beaker and having a volume of about 100 ml, add approximately 0.1 g $(NH_4)_2HPO_4$ and cool the solution to about 10°C.

6.2.6. Add pure aqueous ammonia dropwise until a precipitate forms; allow this to settle and continue to alternate addition of reagent and settling of the precipitate until precipitation is complete as evidenced by no formation of a precipiate on the addition of a drop of aqueous ammonia.

6.2.7. Add 10 ml of aqueous ammonia and allow to stand overnight.

6.2.8. Examine the first filtrate for signs of precipitate. If none, discard the solution; if a small precipitate is present, decant about three quarters of the supernatant solution and filter the rest as previously described.

6.2.9. Transfer the second precipitate to the same paper. Wash beaker(s), precipitate and paper with cold 5% aqueous ammonia as before.

6.2.10. Police the beaker(s) if necessary. Wash the precipitate and paper ten times with aqueous ammonia solution, and once with water. Discard the filtrate.

6.3. Magnesium - Ignition of magnesium ammonium phosphate

6.3.1. Fold the paper lightly (do not make a tight fold because this makes the burning away of the carbon more difficult) and place it in weighed 25 ml platinum crucible.

6.3.2. Wipe the inside of the funnel with a small piece of filter paper and add this to the crucible.

6.3.3. Place the crucible with the cover drawn back slightly, in a cold electric muffle furnace.

6.3.4. Allow the temperature to rise to about 450°C and maintain it at this level until all of the carbon is burned off and the residue is greyish-white in colour. Do not allow the crucible to become even a dull red before this stage is reached, and at no time allow the contents of the crucible to catch fire.

NOTE: When $MgNH_4PO_4$ is ignited, it losses H_2O and NH_3 and leaves a residue of magnesium pyrophosphate, $Mg_2P_2O_7$. Burning off the carbon at a low temperature is very important; otherwise the platinum crucible, if one is used, may be injured and furthermore, it will be impossible to get a residue free from carbon.

6.3.5. Heat the covered crucible and contents at approximately 1100°C for 30 minutes, cool in a desiccator for 30 minutes and weigh as $Mg_2P_2O_7$.

6.3.6. Repeat the ignition, cooling and weighing until constant weight is obtained.

NOTE: The ignited residue may now be corrected for co-precipitated manganese, if this was not removed previously (if it is present). The manganese found is subtracted as $Mn_2P_2O_7$ from the total weight of the pyrophosphate.

NOTE: If Mn is determined in a separate sample using AA, the $Mg_2P_2O_7$ precipitate may be corrected for Mn as $Mn_2P_2O_7$, assuming that all of the Mn was precipitated with the Mg. Another alternative is to determine Mn by AA by dissolving $Mg_2P_2O_7$ precipitate in HNO_3. Impurity of Ca can also be checked in this solution if present by AA.

Conversion Factors:

$$Mg_2P_2O_7 \underset{2.7604}{\overset{0.3623}{\rightleftarrows}} MgO$$

$$Mn_2P_2O_7 \underset{2.0007}{\overset{0.4998}{\rightleftarrows}} MnO$$

$$Mn_2P_2O_7 \xleftarrow[2.5831]{} Mn$$

Quality control:

The determination limit for this method is 0.50% for all oxides. This method is not used on a routine basis and only limited data are available to estimate precision and accuracy. However, a number of Standard Reference Materials (SRMs) have been analyzed by the Laboratories and the data contributed as part of the SRM certification program. In every case the accuracy and precision have been outstanding. Typically, the reported Geoscience Laboratories data have been within 0.2 of the certified value when considered as members of the population of contributed data.

Productivity:

A technician should be able to complete 4 samples per week.

Additional Notes:

1. Beakers, funnels, flasks and other glassware should be cleaned well before use. If greasy, a rinse with chromic acid cleaning solution is desirable. Rinse vessels thoroughly with tap water, and follow with distilled water.

2. Wash solutions of various kinds are called for in the course of the analysis. To save time, special wash bottles containing 2% ammonium nitrate, 5% HCl, 5% ammonia and 0.1% ammonium oxalate solution are kept on hand.

3. All beakers, casseroles, flasks etc., containing solutions being analyzed must be labelled to prevent confusion and mixing of samples.

4. Two points on washing precipitates: (1) There is a danger of losing some of the precipitate if too vigorous a jet from the wash bottle is used; (2) In washing, use small quantities of wash liquid, and let each portion drain through before adding the next.

5. Preliminary heating of a crucible containing a wet paper and precipitate should be very slow until the water is removed, a very gradual increase of temperature follows, until the volatile matter from the paper has been smoked off. During this stage do not allow the gases from the paper to burn with a flame since this may result in drafts and loss of precipitate. Then increase the temperature to a dull red heat until all carbon has disappeared. Never heat strongly while carbon is still present. The crucible is kept only partially covered, to allow entrance of air. During final heating, the crucible is almost fully covered.

6. Hot platinum-ware should always be handled with platinum tipped tongs. Before picking up crucibles etc., with tongs, be sure that the tips of the latter are clean.

6.1 Most stains in platinum can be removed by fusion with little potassium pyrosulphate ($K_2S_2O_7$). After cooling, the pyrosulphate is dissolved in hot water.

6.2 Never allow the blue cone of a flame to touch the platinum crucible being heated. To do so causes formation of platinum carbide, which will eventually ruin the crucible.

6.3 Platinum-ware should be kept well burnished with fine sea-sand. This is important for crucibles which are subjected to long ignitions.

Bibliography:

Outline of methods for the Chemical Analysis of Rocks and Minerals, Department of Mineralogy, University of Toronto.

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DETERMINATION OF TITANIUM AS (TiO_2)

Introduction:

Titanium is recognised as one of the most universally distributed elements and the tenth most abundant in the crust of the earth.

It is present in all igneous, metamorphic, or sedimentary rocks of a more or less siliceous character. Though present even in the most siliceous rocks, it is more abundant in the so called basic silicate rocks.

Chief among its numerous minerals are rutile, octahedrite (anatase), ilmenite, titanite and pervoskite. It is also a component, in smaller amounts, of many pyroxenes, hornblendes, biotites, garnets, and other ferro-magnesian minerals, and is found in some magnetite and hematite.

Owing to the refractory nature of some of its compounds, titanium tends to concentrate in the residual products of decomposition of many rocks. Typically, concentrations in rocks will not exceed 1 percent, but may rise to over 5 percent.

In this method the concentration of titanium is determined by measuring the absorbance of the yellow-coloured complex formed by titanium with hydrogen peroxide in an acidic solution. The measurement is taken by a photometer at wavelength 435 nm.

This method is used where the sample matrix makes titanium unsuitable for determination by XRF. This arises, for example, when the sulphur content of a rock is too high to allow a fused bead to be prepared for XRF determination.

This method is applied when TiO_2 content is 3.0%, and above the existing XRF calibration range (0 to 3.0%).

This method is also applied for very accurate determination, e.g. where a standard reference material has to be analyzed for certification purposes.

Safety advisory:

1. When using HF wear glasses and gloves, and be extremely careful. More information on HF is available in the Geoscience Laboratories' Safety Manual, page IV-17.

Method:

The method consists of the following techniques:

1. Sample decomposition by acid digestion, and followed by residue fusion (if necessary).
2. Measurement of absorbance by developing colour.
3. Calculation of TiO_2 concentration based on a calibration curve produced from known standard solutions

Apparatus:

- Platinum dishes, 50 ml
- Vycor brand glass crucibles, 30 ml
- Volumetric flasks, 100 ml
- Glass funnels, 75 mm
- Filter paper, Whatman No. 42, (12.5 cm)
- Burette 0 to 25 ml
- Baush and Lomb spectronic 501 colorimeter

Reagents:

- Hydrochloric acid, HCl, 36.5% - 38 %
- Sulphuric acid, H_2SO_4, 96%
- Phosphoric acid, H_3PO_4, 85%
- Hydrofluoric acid, HF, 48%
- Potassium pyrosulphate, $K_2S_2O_7$
- Hydrogen peroxide (30%), reagent grade
- Potassium titanium oxalate, $K_2TiO(C_2O_4).2H_20$
- Diammonium sulphate, $(NH_4)_2SO_4$

Procedures:

1. Reagent preparation

1.1. Hydrogen peroxide (3%) solution - Dilute 10 ml of 30% reagent grade hydrogen peroxide to 100 ml with distilled water. Make fresh before use.

1.2. (1:1) H_2SO_4 solution - Add, very carefully, 100 ml of concentrated H_2SO_4 using a graduated cylinder to a 200 ml volumetric flask already containing 75 ml of distilled water and mix.

1.2.1. Immediately immerse the flask in a 800 ml beaker of cold tap water in order to dissipate the heat generated. When cool, make up to 200 ml with distilled water and mix well. Store in a glass bottle.

2. Standard TiO_2 solution preparation (0.5 mg TiO_2/ml)

2.1. Weigh exactly 2.2163 g of potassium titanium oxalate $K_2TiO(C_2O_4).2H_2O$ and transfer quantitatively to a 500 ml Erlenmeyer flask.

2.2. Add 8 g of diammonium sulphate $(NH_4)_2SO_4$.

2.3. Add 100 ml of concentrated H_2SO_4.

2.4. Place a short-stemmed glass funnel in the neck of the flask.

2.5. Gradually heat to boiling, and boil for 5-10 minutes very carefully.

2.6. Continue the heating until complete solution has been effected and no unattacked material remains on the walls of the flask.

2.7. Cool and transfer to a 1000 ml volumetric flask already containing 500 ml of distilled water.

2.8. Wash the Erlenmeyer flask with several portions of 5% H_2SO_4 and finally with distilled water, and transfer all washings into the 1000 ml volumetric flask.

2.9. When cool, make to 1000 ml with distilled water.

3. Sample Decomposition

3.1. Weigh exactly 0.500 to 1.000 g (depending on the amount of TiO_2 present) of sample and transfer to a 50 ml platinum dish.

3.2. Moisten with about 1 ml of distilled water.

3.3. Cover the dish and add 10 ml of concentrated HCl.

3.4. Heat on a hot plate for about 30 minutes.

3.5. When effervescence has ceased, remove and rinse the cover with distilled water, adding washings to the dish.

3.6. Add 10 ml of HF (48%) and 10 ml of 1:1 H_2SO_4.

3.7. Digest and evaporate to dense fumes of SO_3 for 5 minutes.

3.8. Cool, wash the sides and evaporate again to dense fumes of SO_3 for few minutes (2 to 3 minutes). Fluoride ions interfere with the titanium determinations by bleaching the yellow colour. Therefore, it is important to expel fluoride by fuming with H_2SO_4.

3.9. Cool, add 25 ml of distilled water, cover and heat on hot plate until sample is dissolved (30 minutes approximately). If the sample is high in Ca, Ba, and Mg, insoluble sulphates of these elements will be formed and will not be dissolved.

3.10. Filter using Whatman No. 42 (12.5 cm) filter paper in a 100 ml volumetric flask.

3.11. Wash the platinum dish several times with small portions of 5% H_2SO_4 (warm) and transfer all the washings to the filter paper.

3.12. Wash the filter paper several times with small portions of 5% H_2SO_4 wash solution.

3.13. Ensure volume in the 100 ml flask after washings does not exceed 75 ml.

3.14. This is your original solution to develop and measure colour.

4. Measurement of TiO_2 concentration

4.1. Add 5 ml of phosphoric acid (H_3PO_4) to the original solution in 100 ml volumetric flask and shake well (the colour due to ferric sulphate is bleached by the addition of phosphoric acid).

4.2. Add 10 ml of 3% solution (made fresh) of hydrogen peroxide (H_2O_2), mix and make up to 100 ml with distilled water.

4.3. Measure the absorbance due to the yellow-coloured complex formed by titanium with hydrogen peroxide in acid solution at 435 nm in a cell against a blank reagent containing 10 ml of (1:1) H_2SO_4.

5. Calculation of the results

5.1 To a series of 100 ml volumetric flasks add 10 ml of (1:1) H_2SO_4 and dilute with distilled water to about 50 ml.

5.2. Add from a burette (0-25 ml), a series of aliquots of the standard TiO_2 solution (0.5 mg TiO_2/ml) to give 0.50, 1.00, 2.00, 4.00, 8.00 and 10.00 mg TiO_2/100 ml and mix.

5.3. Add 5 ml of phosphoric acid (H_3PO_4) using a fast draining pipette and mix.

5.4. Add 10 ml of 3% H_2O_2 solution (made fresh) using a pipette mix and make it to 100 ml with distilled water and shake well.

5.5. Measure the absorbance of the yellow-coloured complex formed by the titanium with hydrogen peroxide in acid solution at 435 nm in a cell against a blank having all the reagents and 10 ml of (1:1) H_2SO_4.

5.6. Make a calibration curve.

5.7. The curve should be linear.

5.8. The yellow-coloured complex is very stable and reproducible.

5.9. Use the relative absorbance of the sample at 435 nm to obtain the concentration of TiO_2 per 100 ml of solution from the calibration curve.

$$\%TiO_2 = \left(\frac{mg\ TiO_2}{ml}\right) x \frac{1}{1000} x \frac{100}{sample\ weight}$$

Quality Control:

The determination limit for this method is 0.02% TiO_2. There is not enough data available to establish precision and accuracy for this method. An estimate of precision at 95% confidence limit (2σ) for a mid-range value is ± 0.1% (absolute), with a mid-range value of 0.5%. The accuracy would be similar to this value for SRMs.

Productivity:

A technician should be able to complete 15 determinations per day.

Additional Notes:

1. Samples high in sulphur should be roasted first in a Vycor brand glass crucible (30 ml) in a furnace at 650°C for 3 hours or preferably overnight, then transfer the powder from the crucible to a platinum dish. Rinse the crucible with several portions of distilled water and finally with concentrated HCl into the dish.
2. Titanium minerals are considerably more resistant to decomposition than the silicate matrix in which they occur. Care must be taken to ensure that the mineral grains are completely attacked.
3. Any residue (which could contain such minerals as rutile and ilmenite) should be fused with small amount of potassium pyrosulphate ($K_2S_2O_7$) in Vycor brand glass crucible (30 ml).
4. The residue, and the filter paper from filtration of the digested sample solution, should be ignited in a Vycor brand glass crucible using a muffle furnace. Start with a cold furnace and burn off the paper allowing the temperature to rise slowly. Ignite the residue for about 5 minutes at 600°C. Then fuse with potassium pyrosulphate (100 to 300 mg depending upon the amount of residue present). After leaching the fused matter in 5% H_2SO_4 tranfer to a 100 ml volumetric flask and develop the colour as per procedure.
5. A number of other metals form coloured complexes with hydrogen peroxide including vanadium, uranium, niobium, molybdenum, and, under certain circumstances, chromium.
6. Presence of alkali salts causes slight bleaching effect - the bleaching action of alkali salts is less in a 10% (by volume) solution of H_2SO_4 than in one containing 5%.
7. In titanium solutions a moderate amount (10-20%) of acid must be present to prevent precipitation of titanium by hydrolysis.

Bibliography:

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Jeffery, P.G., Chemical Methods of Rock Analysis, 3rd Edition, 1981, 379 pages.

Maxwell, J.A., Rock and Mineral Analysis, Wiley Interscience Publishers, 1968, 584 pages.

Potts, P.J., A Handbook of Silicate Rock Analysis, Blackie and Sons Ltd., Glasglow, 1987, 622 pages.

DETERMINATION OF PHOSPHORUS (P_2O_5) COLORIMETRIC METHOD

Introduction:

The determination of phosphorus, usually present in the range 0.1% - 0.5% P_2O_5, is a necessary part of any silicate rock analysis.

In silicate rocks and minerals the phosphorus is usually present as orthophosphate (apatite is the most common mineral). Phosphorus is also an essential constituent of living matter. The average natural crustal abundance of phosphorus in igneous rock is approximately 1200 ppm. Limestone and sandstone contain rather less phosphorus than igneous rocks. A few hundred parts per million being typical. Deep-sea sediments contain up to a few thousand parts per million P_2O_5.

In this method, the concentration of phosphorus is determined by measuring the absorbance of the yellow-coloured molybdovanadophosphoric acid complex, produced by adding ammonium vanadate and ammonium molybdate to the sample. The measurement, by a photometer, is taken at wavelength 460 nm.

This method is used only where the sample matrix makes determination by XRF unsuitable e.g. when the sulphur content of the rock is too high to allow a fused bead to be prepared for XRF determination.

This method is also applied when the P_2O_5 content is > 1.0%, and beyond the calibration range (0 - 1.0%) of the current XRF method.

This method is used for accurate determinations such as where a standard reference material has to be analyzed for certification purposes.

A preliminary separation of phosphorus is sometimes made to eliminate the interference of elements such as copper, nickel and chromium, which form coloured solutions. Presence of titantium phosphate can cause dissolution problems.

Safety advisory:

1. When using HF wear glasses and gloves, and be extremely careful. More information on HF is available in the Geoscience Laboratories' Safety Manual, page IV-17.

Method:

The method consists of the following techniques:

1. Sample decomposition by acid digestion with residue fusion (if necessary).
2. Measurment of absorbance by developing colour.
3. Calculation of P_2O_5 concentration based on a calibration curve produced by known standard solutions.

Apparatus:

- Platinum or teflon dishes, 50 to 100 ml (teflon dishes are preferred due to lower cost, and for higher productivity)
- Glass volumetric flasks, 100 ml
- Glass funnels, 75 mm
- Filter paper, Whatman No. 40 and No. 42 (12.5cm)
- Baush and Lomb spectronic 501 colorimeter
- Micro-burette, 0 - 10 ml

Reagents:

- Ammonium molydate, $(NH_4)_6Mo_7O_{24}.4H_2O$
- Ammonium metavanadate, NH_4VO_3
- Boric acid crystals, H_3BO_3
- Nitric acid, HNO_3, 69.0 - 71.0%
- Hydrofluoric acid, HF, 48%
- Potassium phosphate monobasic, KH_2PO_4

Procedures:

1. Reagent preparation

1.1.1. Ammonium molybate (5%) stock solution - Dissolve 50 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ in approximately 500 ml of warm distilled water, and let stand for several hours.

1.1.2. Filter through a 12.5 cm Whatman No. 42 filter paper.

1.1.3. Dilute to 1 liter with distilled water and store in a polyethylene bottle.

1.2.1. Ammonium Metavanadate (0.25%) stock solution - Dissolve 2.5 g of NH_4VO_3 in 500 ml of hot distilled water.

1.2.2. Cool and add 20 ml concentrated HNO_3.

1.2.3. Let stand for several hours, and filter if not clear.

1.2.4. Dilute to 1 liter with distilled water.

1.2.5. Store in a glass bottle.

1.3.1. Boric Acid (H_3BO_3) 4.5% stock solution - Dissolve 45 g in distilled water by heating slowly.

1.3.2. When dissolved, cool and make to 1 liter with distilled water.

1.3.3. Store in a polyethylene bottle.

2. Standard P_2O_5 solution preparation (1.00 mg P_2O_5/ml)

2.1. Weigh exactly 0.959 g of potassium phosphate monobasic (KH_2PO_4) dried at 100°C.

2.2. Transfer to a 100 ml glass beaker.

2.3. Dissolve in distilled water. Potassium phospate monobasic should be soluble without heating.

2.4. Transfer to a 500 ml volumetric flask quantitatively, washing beaker with several small portions of distilled water.

2.5. Make to volume with distilled water.

2.6. Store in a tightly capped polyethylene bottle. (It is always a good practice to store standard solutions in a tightly capped bottle to minimize evaporation of the solution)

3. Sample decomposition

3.1. Weigh exactly 1.000 g of sample and transfer to a 50 ml teflon dish.

NOTE: Since the presence of P_2O_5 in rock samples is usually in the range of 0.1 - 0.5%, a 1.000 g sample can be used. If P_2O_5 is in a greater concentration, less sample may have to be used.

3.2. Moisten with distilled water.

3.3. Cover the dish and add 10 ml of concentrated HNO_3.

3.4. When effervescence has ceased, remove and rinse off the cover.

3.5. Add 10 ml of 48% HF.

3.6. Place the dish on a hot plate and slowly evaporate the contents to dryness.

3.7. Cool, moisten with distilled water, add 5 ml of concentrated HNO_3 and 5 ml of HF; and again evaporate to dryness.

3.8. Cool, add 20 ml of HNO_3 (1:1) and again evaporate to dryness.

3.9. Heat the contents of the dish for a further 30 min. after the salts appear to be dry.

3.10. Cool, add 20 ml (1:1) HNO_3 (previously boiled and cooled to remove oxides of nitrogen).

3.11. Add 10 ml of (4.5%) boric acid solution.

3.12. Cover and digest the contents on a hot plate, until dissolution appears to be complete.

3.13. Filter through a 12.5 cm Whatman No. 40 paper into a 100 ml volumetric flask.

3.14. Police the dish and wash with distilled water having a few drops of colourless (1:1) HNO_3. Transfer all washings to the filter paper.

3.15. Wash the filter paper several times with distilled water having few drops of colourless (1:1) HNO_3.

3.16. After filtration and washings, make to volume in a 100 ml volumetric flask with distilled water. This is your original solution.

4. Measurement of P_2O_5 concentration

4.1. Pipet a 50 ml aliquot into a 100 ml volumetric flask from the original solution. The splitting of the original solution (100 ml) may be done with a dry pipette or conveniently as follows:

4.1.1. Rinse a clean pipette with the original solution and transfer the rinsings to a 150 ml beaker.

4.1.2. Pipet a 50 ml aliquot into a 100 ml volumetric flask, then rinse the pipette with water into the beaker.

4.1.3. Transfer the solution in the beaker to the 100 ml flask of the original solution.

4.1.4. Dilute to 100 ml and use for correcting the absorbance due to the presence of other coloured substances.

4.2. Add 10.0 ml of ammonium vanadate solution by pipette to the solution from step 4.1 and mix.

4.3. Add 20.0 ml of ammonium molybdate solution by pipette and mix.

4.4. Mix, dilute to volume, and mix thoroughly again. Allow to stand for 30 minutes.

4.5. Measure the absorbance of the yellow colour complex (molybdovanadophosphoric acid) at 460 nm in a cell, against a blank consisting of the reagents and 10 ml of (1:1) HNO_3 already boiled, cooled and colourless.

4.6. Use the other 50 ml portion of the original solution to correct the absorbance due to the presence of other coloured sustances as explained in step 4.1.4.

5. Calculation of the results

5.1. To a series of 100 ml volumetric flasks, add from a micro-burette, a series of aliquots of the standard phosphate solution (1.00 mg P_2O_5/ml) to give 0.50, 1.00, 2.00 and 2.50 mg P_2O_5/100 ml.

5.2. Add 10 ml of (1:1) HNO_3, already boiled and colourless.

5.3. Dilute to about 50 ml with distilled water.

5.4. Add by pipette 10 ml of ammonium vanadate solution and mix.

5.5. Then add by pipette 20 ml of ammonium molybdate solution and mix.

5.6. Dilute to 100 ml and mix thoroughly. Allow to stand for 30 minutes.

5.7. Measure the absorbance of the yellow complex at 460 nm for each solution against the solution containing all the reagents with 10 ml colourless (1:1) HNO_3.

5.8. Prepare a calibration curve using the absorption reading on each solution versus concentration.

5.9. The curve should be linear up to 2.5 mg P_2O_5/100 ml.

5.10. The yellow complex is stable for at least one day.

5.11. Measure the absorbance of the samples at 460 nm and obtain the concentration of P_2O_5 per 100 ml of solution from the calibration curve.

$$\% \ P_2O_5 = (mg\ P_2O_5/100\ ml) \times \frac{1}{1000} \times \frac{100}{sample\ wt.}$$

Quality Control:

The determination limit of this method is 0.02% P_2O_5 using a 1.000 g sample.

The mid-range value is 0.5%, and an estimate of precision, at 95% confidence limits (2σ), at the mid-range value is 0.1% (absolute).

Accuracy is similar to precision for this method.

Productivity:

A technician should be able to complete about 10 determinations per day.

Additional notes:

1. Samples high in sulphur should be roasted first in a Vycor brand 30 ml glass crucible in a furnace at 650°C for 3 hours or preferably overnight. Then transfer the powder from the crucible to the platinum or teflon dish. Rinse the crucible with several portions of water and finally with HNO_3 into the dish.

2. If the residue on the filter paper after filtration of the digested sample solution shows white - no gritty residue - the residue may be titanium phosphate.

   If the residue amounts to more than a few grains, it should be ignited in a platinum crucible and fused with 0.5 g of anhydrous Na_2CO_3. The cake is leached with water and HNO_3, filtered and added to the volumetric flask having the original solution.

3. Iron interference is negligible at 460 nm.

4. Sample blank absorbance correction is necessary in the presence of other coloured substances. (Solutions should be white after decomposition).

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Maxwell, J.A., Rock and Mineral Analysis, Wiley Interscience Publishers, 1968, 584 pages.

Potts, P.J., A Handbook of Silicate Rock Analysis, Blackie and Sons Ltd., Glasglow, 1987, 622 pages.

DETERMINATION OF SODIUM AND POTASSIUM
FLAME PHOTOMETRIC METHOD

Introduction:

All silicate rocks and minerals contain both sodium and potassium in amounts varying from less than 100 ppm in some ultrabasic rocks such as dunite and peridotite, to as much as 10 percent K_2O or 15 percent Na_2O in feldspar minerals.

Rocks containing large amounts of potassium or sodium are rare, and most silicate rock specimens contain both alkalies in somewhat similar amounts in the range of 1-6 percent Na_2O and 0.5-6.0 percent K_2O.

Both elements occur as major constituents of many rock-forming minerals, particularly the alkali feldspar group, and are always determined where a complete chemical analysis of a silicate rock or mineral is required.

This method is used only where the sample matrix makes the constituents concerned unsuitable to be determined by XRF. This will arise when the sulphur content of the rock is too high to allow a fused bead to be prepared by XRF.

This method is also applied for accurate determination where a standard reference material has to be analysed for certification purposes. The method is applicable to most rock samples where Li is present in trace amounts (0 - 100 ppm).

A compound heated in a flame dissociates and the excited ions emit light of a characteristic wavelength. The intensity of a given wavelength is proportional to the concentration of the source ion. In the flame photometer, the light produced falls on narrow-band filters which reject all but the pertinent wavelengths. These are transmitted to individual phototubes whose electrical outputs vary with light intensity, and hence provide a measure of ion concentration.

Absolute measurements of light intensity by this method are affected by variations in flame condition and aspiration rate. Sodium and potassium measurements therefore require the introduction of another ion in a known concentration to provide a reference level. Lithium is chosen because it emits light of a suitable wavelength and is not present in significant concentrations in most rock samples.

The three electrical outputs are combined to produce two signals, one proportional to the ratio of concentration of Na/Li and the other K/Li. These signals are presented in digital form and the resulting readout indicates absolute concentrations of sodium and potassium expressed in millequivalent per liter.

Safety advisory:

When using HF wear glasses and gloves, and be extremely careful. More information on HF is available in the Geoscience Laboratories' Safety Manual page IV-17.

When using perchloric acid use fume hood designed for perchloric acid fumes.

Method:

The method consists of the following techniques:

1. Sample decomposition by acid digestion
2. Simultaneous measurement of Na and K using Flame Photometer type FLM2.
3. Calculation of Na and K concentrations based on a calibration curve produced from known standard solutions

Apparatus:

- Platinum dishes, 50 - 100 ml
- Glass funnels, 75 mm
- Filter paper, Whatman No. 40 (12.5 cm)
- Glass volumetric flasks, 250 ml
- Vycor brand glass crucibles, 30 ml
- Polypropylene beakers, 5 ml
- Flame photometer type FLM2, by Bach-Simpson Ltd. London, Ontario

Reagents:

- Lithium carbonate, Li_2CO_3, reagent grade
- Sodium chloride, NaCl, reagent grade
- Potassium chloride, KCl, reagent grade
- Concentrated hydrochloric acid, HCl, 36.5 - 38%
- Concentrated perchloric acid, $HClO_4$, 60%
- Concentrated sulphuric acid, H_2SO_4, 96%
- Concentrated hydrofluoric acid, HF, 48%

- Sterox SE, non-ionic wetting agent (for use in Flame Photometer)

Procedures:

1. Reagent preparation

1.1. 1% Sterox SE (non-ionic wetting solution) - Add 10 ml of Sterox SE solution to a 1 liter flask and make to volume with distilled water.

1.2. Li Stock Solution (1500 meq/l) - Weigh accurately 55.4175 g of Li_2CO_3 and transfer to a clean 1 liter glass beaker. (There is no need to dry Li_2CO_3 since the standards and blanks are prepared in the same fashion)

1.2.1. Cover with a clean watch glass and add about 100 ml of distilled water.

1.2.2. Add, caustiously, small portions of 200 ml conc. HCl.

1.2.3. Once the effervescence has stopped and dissolution is complete, cool and transfer quantitatively to a 1 liter volumetric flask by washing the beaker with several small portions of distilled water.

1.2.4. Add 10 ml of 1% Sterox SE solution, mix and make to volume (1 liter) with distilled water. Store in a polyethylene bottle.

1.3.1. Preparation of (1:1) H_2SO_4 solution - Add very carefully 100 ml of conc. H_2SO_4 using a graduated cylinder to a 200 ml volumetric flask already having approximately 75 ml of distilled water and mix.

1.3.2. Immediately immerse the flask in a 600 ml glass beaker or tray containing cold tap water as the solution will be very hot due to the reaction.

1.3.3. When cool, make to volume with distilled water and store in a glass bottle.

2. Standard Na and K solution preparation (1000 ppm Na and K)

2.1. Weigh exactly 2.5423 g of NaCl (dried at 105°C) and transfer quantitatively to a clean 250 ml beaker

2.2. Weigh exactly 1.9069 g KCl (dried at 105°C) and transfer quantitatively to the 250 ml beaker containing the NaCl.

2.3. Dissolve in about 150 ml distilled water.

2.4. Transfer to a 1 liter volumetric flask quantitatively by washing the 250 ml beaker several times with small portions of distilled water.

2.5. Make to volume (1 liter) with distilled water. Mix well and store in a polyethylene bottle.

3. Sample decomposition

3.1. Weigh exactly 0.125 g of sample and transfer to a 50 ml platinum dish.

3.2. Moisten with about 1 ml of distilled water.

3.3. Cover the dish with a watch glass (if carbonate is present) and add 5 ml of conc. $HClO_4$.

3.4. When effervescence has ceased, remove and rinse off the cover in the dish with distilled water.

3.5. Evaporate to complete dryness on a hot plate.

3.6. Cool, add 10 ml of conc. HCl, 5 ml of HF (48%) using plastic graduated cylinder and 2 ml of 1:1 H_2SO_4 (using a pipette).

3.7. Allow to go into solution at a moderate heat and take down to a low volume (approximately 10 ml).

3.8. Add another 5 ml of conc. HCl and 5 ml of HF (48%).

3.9. Evaporate to complete dryness (until no more fumes of SO_3 are visible).

3.10. In order to remove the last traces of SO_3, hold platinum dish using platinum tipped tongs and heat very carefully with a Meker burner until the reappearance of SO_3 fumes and finally heat strongly with full flame until all fuming ceases. This helps in removing the last traces of HF and converting sulphates of many elements into oxides.

3.11. Cool the dish and add about 5 ml of conc. HCl.

3.12. Evaporate to dryness on a low heat. This helps in converting oxides to chlorides which are easily soluble in distilled water.

3.13. Cool and add about 5 ml of conc. HCl. Leave it for about 1-2 minutes to react.

3.14. Then add about 30 ml of distilled water and heat well until sample is in solution. It takes approximately 45 minutes to one hour depending upon the nature of the sample.

3.15. Filter into a 250 ml volumetric flask using a Whatman No. 40 filter paper.

3.16. Wash the platinum dish several times with small portions of hot distilled water (using glass wash bottle) and transfer all washings to the filter paper.

3.17. Wash filter paper several times with small portions of hot distilled water (using glass wash bottle).

3.18. Finally, add 2.5 ml of Li stock solution (1500 meq/l) and make to 250 ml with distilled water in a volumetric flask. Now the solution is ready for measurement.

4. Addition of reference Li stock solution

4.1.1. Preparation of Na and K standard solution for calibration - Add 0 ml, 1.25 ml, 2.5 ml, 5.0 ml and 7.5 ml and 10.0 ml from microburette (0 - 10 ml) of 1000 ppm Na and K stock solution into 500 ml volumetric flasks.

4.1.2. Add 5 ml (using a 0 -10 ml microburette) of Li stock solution (1500 meq/l) to each of the 500 volumetric flasks.

4.1.3. Make to volume (500 ml) with distilled water. Mix well, transfer to the polyethylene bottles and store.

4.1.4. This will give a concentration of 0, 2.5, 5, 10, 15 and 20 ppm Na and K in the solution. Calibration solutions are stable.

4.2. Preparation of Li blank/diluent

4.2.1. Add 5 ml (using a 0 - 10 ml microburette) of Li stock solution (1500 meq/l) into a 500 ml volumetric flask and make to volume with distilled water.

4.2.2. Mix well and store in a polyethylene bottle.

4.2.3. This is the lithium blank/diluent which is used to centre lithium standard meter and also to set Na and K, zero on the instrument.

5. Measurement of Na and K concentrations

5.1. Starting up

5.1.1. Set the 'Display' switch to 'Continuous'.

5.1.2. Check the drain line is filled with water. If in doubt, inject a few milliliters of distilled water into the drain tube outlet and allow the excess to drain off.

5.1.3. Open the valve at the top of the propane cylinder one full turn only.

5.1.4. If a central air supply is being used, open the air valve.

5.1.5. If the air filter is fitted with a manual drain ensure this is closed.

5.1.6. Remove distilled water cup from the sample tray.

5.1.7. Switch on power.

5.1.8. Check gas, air and flame indicator lamps are lit in sequence. If any of the above fail to occur, gas and air supplies will be automatically shut down and the ignition spark will stop after 10 seconds. Turn off the power, wait a few seconds, and turn on again. If the flame photometer again fails to ignite, refer to the installation and maintenance manual.

5.1.9. Place a plastic cup (30 ml) filled with lithium blank/diluent solution on the sample tray. Raise the tray to the limit of its travel. Continue to aspirate lithium for 10 minutes or until the inside of the atomizer chamber is thoroughly wetted. Refill the cup as necessary.

5.2. Zero setting and calibration

5.2.1. Set the "K" range to "200". Leave on "Display" switch set to "continuous".

5.2.2. Aspirate Li blank solution.

5.2.3. Unlock the "Set Li Standard" control at lower right by turning the base of the control knob counter clockwise.

5.2.4. Set the "lithium standard" meter to the centre of the green band.

5.2.5. Relock the control by turning the base carefully clockwise as far as it will go.

5.2.6. Unlock the Na and K zero controls and adjust them until both indicators read "000". A reading of "999" indicates that the setting is below zero, and the appropriate control should be carefully turned clockwise until the reading is "000". Relock both controls.

5.2.7. Remove the lithium blank solution cup.

5.2.8. Insert a fresh sample of the desired Na-K standard.

5.2.9. Verify that the "lithium standard" meter reads in the centre of the green band. Readjust if necessary using "Set Li standard" control.

5.2.10. Using the Na and K "Cal" controls, adjust the two readouts to values corresponding to the standard being aspirated (first start with 15 ppm adjusting to read 150 on read out). Then adjust the values for other standards.

NOTE:

1. Insert the standard every tenth determination to check calibration.
2. Steps 5.2.1 to 5.2.10 should be repeated every 30 minutes or less as the user determines on the basis of experience.

5.3. Run samples

5.3.1. Remove the Na/K standard.

5.3.2. Place a sample cup of unknown on the sample tray.

5.3.3. Raise the tray to the limit stop. The "display" switch can be left set to "continuous", which allows a sample to be monitored as long as sufficient fluid remained in the sample cup. Readings can be taken when the operator feels that they have reached stability, usually 10-12 seconds after insertion of the sample. Alternatively, the operator can set the mode switch to "Delayed Hold". In this condition, raising the sample tray initiates a timed sequence in which the readouts indicate freely for 15 seconds, allowing time for both Na and K readings to stabilize. After this delay the readings are "held". Loss of reading will not occur until the sample tray is lowered and raised again.

6. Calculation of the results

6.1. Calculation of results is based on 0.125 g sample weight which is made to 250 ml.

$$\%\ Na_2O = (\mu g\ Na/ml)\ x\ \frac{250}{sample\ wt.}\ x\ \frac{100}{10^6}\ x\ 1.3480$$

$$\%\ K_2O = (\mu g\ K/ml)\ x\ \frac{250}{sample\ wt.}\ x\ \frac{100}{10^6}\ x\ 1.2046$$

7. Shutting down

7.1. Aspirate distilled water for ten minutes. It is important that this be done consistently because it will normally make it unnecessary to clean the atomizer chamber. If however, the chamber does become clouded, wash it with soap and water only

7.2. Close gas tank and wait for flame lamp to extinguish.

7.3. If a manual drain is fitted to the air filter, open this and allow condensed moisture to blow off.

7.4. Turn power off.

7.5. If central air supply is being used, close the air valve.

7.6. Place cup of distilled water on the sample tray and leave aspirator needle immersed.

8. Maintenance

8.1. Clean aspirator tube weekly. Use filament provided.

8.2. Clean glass chimney monthly. Wash with detergent. Check light filters at the back of the chimney compartment. Wipe with lense paper.

8.3. Check burner for encrustation. Clean when required.

8.4. Check aspirator rate frequently, 1.5 - 1.7 ml / min.

8.5. Bleed moisture off compressor periodically.

Quality control:

The determination limits are 0.15% for Na_2O and 0.12% for K_2O using a 0.125 g sample and making to 250 ml.

Only limited quality control data are available for the estimation of accuracy and precision.

The Geoscience Laboratories has participated in a number of certification programs and SRMs - SY-2, SY-3, MRG-1, AL-1, AN-G and BEN have been analysed using this method. The results (Table NAK1) are consistent with an estimated precision, at the 95% confidence limit (2σ), at a mid-range value, of 0.4% (absolute).

Table NAK1. Na_2O and K_2O Values for SRMs Obtained By Using Li as an Internal Standard

SRM	Na_2O %		K_2O %	
	GLOGS	Lit.	GLOGS	Lit.
SY-2	4.34	4.31	4.64	4.45
SY-3	4.20	4.14	4.24	4.20
MRG-1	0.77	0.73	0.17	0.18
AN-G	1.73	1.63	0.19	0.13
BEN	3.36	3.18	1.44	1.39
AL-1	10.66	10.59	0.14	0.14
NBS-91	8.47	8.48	3.28	3.25
NBS-70A	2.48	2.55	11.7	11.8

Productivity:

A technician should be able to complete 10 samples per day.

Additional Notes:

1. Samples high in sulphur should be roasted first in Vycor brand glass crucibles, 30 ml, in a furnace at 650°C for 3 hours or preferably overnight. Then transfer the powder quantitatively from the crucible to the platinum dish. Rinse crucible with several portions of distilled water and finally with HCl into the dish.
2. This method is applicable to most of the rock samples where Li is present in trace amounts (0 - 100 ppm). Rocks containing large amounts of Li are rare.

Bibliography:

Jeffery, P.G., Chemical Methods of Rock Analysis, First Edition, 1970

Maxwell, J.A., Rock and Mineral Analysis, Wiley Interscience Publishers, 1968, pp. 405.

Instruction Manual for the Flame Photometer Model FLM2 (December 1970) Bach-Simpson Ltd. 1255 Brydges St. London, Ontario

DETERMINATION OF ±WATER COMBUSTION/INFRARED ABSORPTION METHOD

Introduction:

Water exists in two main forms in rock samples: hydroscopic and structural. Hydroscopic (sorbed) water can be driven off by heating the powdered sample at 105°C to constant weight (2-3 hours).

Hydroscopic water is generally reported as H_2O^- and structural (also called crystalline) water is reported as H_2O^+.

A Leco RMC-100 water determinator is used to rapidly determine both hydroscopic and structural (crystalline) water. The sample is weighed and loaded into the instrument at 105°C. Free moisture (H_2O^-) is driven from the sample in a stream of nitrogen which is monitored in an infra red cell. Water vapour absorbs infra red radiation. The instrument collects the signal and converts it to appropriate units. The displayed signal is in units of weight percent.

A source of determinate error associated with the determination of ± water is that hydrated minerals like talc, topaz, staurolite, cordierite, and epidote do not decompose at temperatures below 1200°C.

Safety advisory:

Protective gloves should be worn, or tongs used, to protect hands from hot sample vessels and when using magnesium perchlorate.

Method:

The method consists of the following techniques:

1. Separation of the water by heating
2. Detection of the water by monitoring the absorption of infra-red radiation by the H_2O molecules
3. Calculation of final result (% H_2O) based on a calibration using standards of known composition.

Apparatus:

- Leco RMC-100 Moisture Determinator
- LB-80 Electronic Balance
- Cylinder of nitrogen with regulator capable of accurately delivering N_2 at pressures of 30 to 50 psi
- Nickel boats
- Tongs
- Push rod
- Glass wool
- Hi vacuum grease
- Brush
- Spatula

Reagents:

- Anhydrone (magnesium perchlorate)

Procedures:

1. Instrumental Analysis

1.1. Turn 'gas on' switch to 'off'.

1.2. Turn on nitrogen supply and set regulator to 40 psi.

1.3. Switch power to 'on'. The 'message centre' will display "POWERUP DIAGNOSTIC" while the instrument performs a diagnostic test.

1.4. After completing the test the message centre will display "ENTER TIME AND DATE Hr/Min Mo/Dy/Yr". Using 24 hour time, enter the correct time and date. Use the number keys on the instrument and push "ENTER" after the information has been keyed in.

1.5. Switch on front panel gas and adjust the Purge flowmeter to 3 litres per minute.

1.6. Switch the Pump on and ensure that the Analysis rotameter is set to 1 litre per minute.

1.7. Press System Update key; then press the YES key.

1.8. Allow 1/2 hour for warm-up.

1.9. Run 2 reference samples. Typical reference materials are MRB-7 and MRB-10 which contain 2.31% and 11.7%, respectively, $+H_2O$. If the results from these analyses are not within ±5% (i.e. 2.20% - 2.43%) of the expected values, re-standardize the instrument and rerun the reference materials.

1.10. Run a blank.

1.11. Run the samples. The run should consist of: Blank, Reference-1, Reference-2, 10 samples, Reference-1, Reference-2,.... Random duplicates should be analyzed every 20 samples or at least once for sample batches of less than 20 samples.

2. Maintenance

2.1. Anhydrone should be replaced when signs of moisture are evident in glass cylinders.

2.2. After 8 hours use, the furnace and quartz wool filter should be cleaned by initiating the self-clean cycle. Cleaning takes about 1/2 hour. (cf Leco Manual; Quick Access #4 p S10).

Quality Control:

Quality is controlled by running reference materials at the beginning of the run and after every 10 samples. If the results from these analyses are not within 5% (relative) of the expected values, re-standardize (Leco manual: Quick Access #3 p.28). Analysis of random duplicates is performed at least once during each run.

The method has been adopted directly from the Leco instrument manual. Additional information is available in the literature and in Potts.

The optimum working range is 0.10% to 10% H_2O. The precision (%RSD) over this range is 2.5% - 3.0%.

Based on 0.5 g sample weight the determination limit for hydrated and structural water are 0.05% and 0.10% respectively.

The method should be accurate to within ±0.01% or ±5.% of the observed value, whichever is greater. The sensitivity of the method is 0.01%.

Validity of Method

Data generated by this method (Leco) were compared with data produced by an established method (Gravimetric). Regression analysis yielded a linear graph with slope close to unity and intercept close to zero. This indicates that the two methods are equivalent and supports the contention that significant sources of determinate error are not biasing the results.

Accuracy: Comparison with Established Method

Comparison of LECO RMC-100 with Gravimetric Procedure (H_2O^+)

Sample	Leco %H_2O^+	Gravimetric %H_2O^-
104	3.13	3.06
117	4.40	4.14
118	4.79	4.61
119A	4.16	4.00
119B	0.90	0.77
121	2.52	2.60
124	1.55	1.54
125	3.21	3.13
132	1.70	1.58
158	1.80	1.76
182	2.07	2.00
199	3.99	3.76
200	2.80	2.82
01	3.09	3.06
22	2.79	2.61
214	2.86	2.71
215	2.74	2.90
218	2.71	2.56
219	3.21	2.91
104D	3.32	3.16
219D	3.07	3.03

Regression Output:

Constant	0.039
Std Err of Y Est	0.103
R Squared	0.988
No. of Observations	21
Degrees of Freedom	19
X Coefficient(s)	0.952
Std Err of Coef.	0.024

These data are plotted on the accompanying graph.

Accuracy was further checked by analyzing standard reference materials.

Accuracy: Typical Analysis of SRM:

STD	H_2O^- *	H_2O^+	Lit. Value (H_2O^+)
NIM-L	0.19	2.24	2.31
NIM-L	0.26	2.24	2.31
NIM-L	0.27	2.28	2.31
MRB-10	0.46	11.74	11.7
MRB-10	0.45	11.85	11.7

* Note: Accuracy statements do not apply to H_2O^- as samples absorb variable amounts of this water.

Results indicate good agreement between observed and expected H_2O^+ values.

Factors such as frequency of standardization, stability of standards and personal determinate error will determine the accuracy of particular determinations. The above data support the contention that accuracy can be expected to be within ±5% of the true value, during routine analysis and at levels significantly above the determination limit.

Productivity:

A technician should be able to complete 30 samples per day.

Additional Notes:

1. While analyzing a sample, the instrument can store the weights of as many as three samples which are queued for analysis.
2. Leave analyzer power on at all times.
3. Alarms : refer to section P. S5 of the manual (1). The most common is "MGT TIMEOUT", which signifies that the analysis has exceeded 800 seconds (this is usually due to the presence of high levels of carbonates). If this occurs, repeat the analysis using V_2O_5. This procedure is similar to the procedure in the absence of vanadium pentoxide, except that V_2O_5 powder is placed on top of the rock powder. A vanadium pentoxide blank should be carried through the analysis and the value obtained should be subtracted from the sample results. NOTE: Do not reuse nickel crucibles if V_2O_5 was employed. The reuse of these crucibles reduces the life of the combustion tube.
4. The RMC-100 can be calibrated using the standards supplied by Leco; $Ca(OH)_2$ and CaC_2O_4, which contain 24.0% and 12.2% respectively $+H_2O$. In-house reference rocks; MRB-10, 7, 14 which contain 11.7%, 2.31%, 2.77%, 2.31% respectively $+H_2O$, can also be used to standardize the instrument.
5. Anhydrone should be sieved through 8 mesh screen.

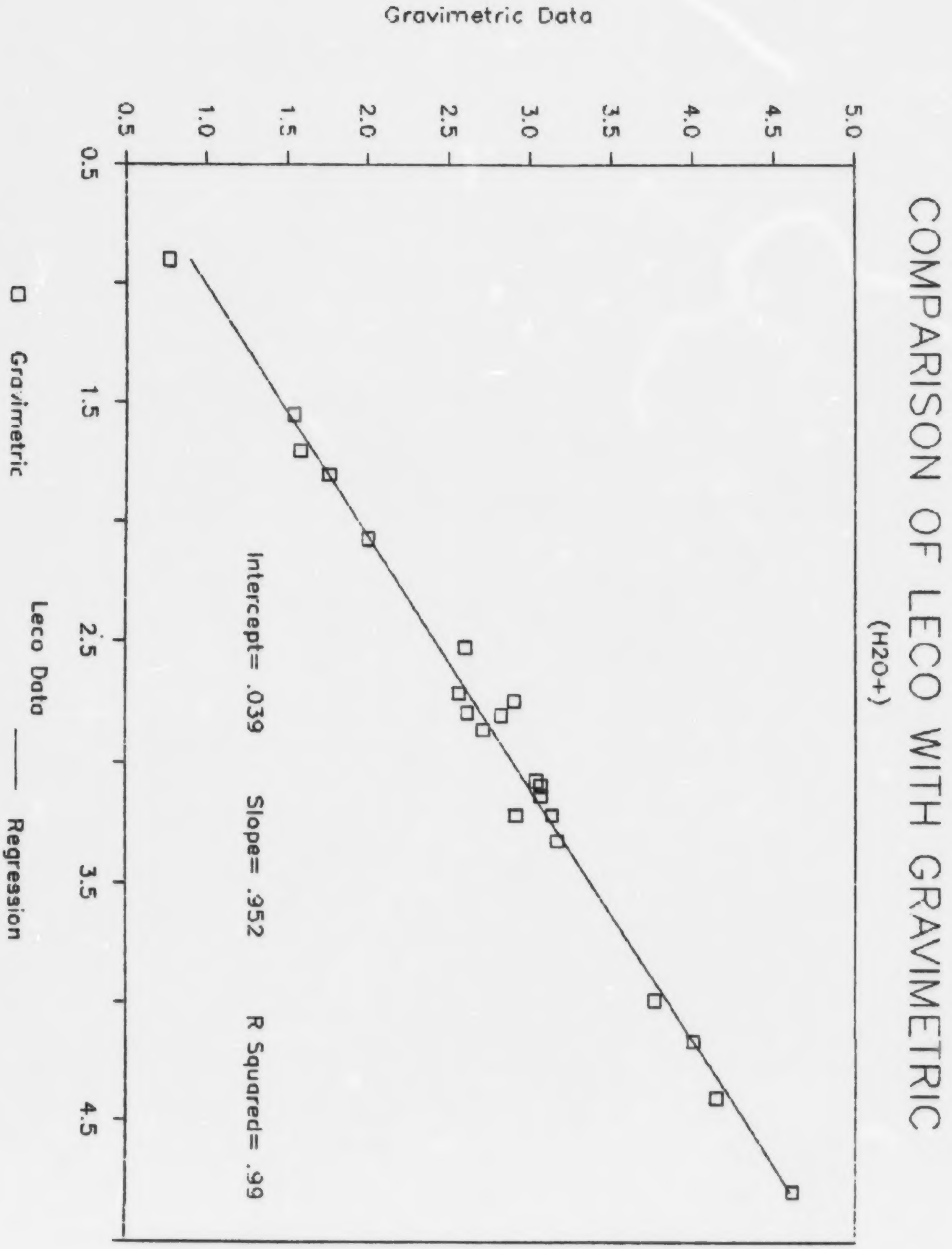
Bibliography:

Leco RME-100 Instruction Manual #601-300. Leco Instruments 5151 Everest Drive Mississauga Ontario L4W 2R2 (phone; 416 624-6933).

Abbey, S., 1980, Simultaneous Determination of Water, CO_2, and S in rocks by volatilization and non-dispersive Infra-red Absorptiometry, Can. Journal of Spectroscopy V. 25, No. 5.

Potts, P., Handbook of Silicate Rock Analysis, Blackie, Glasgow, 1987, pp 70 - 74.

Shapiro, L., Rapid Analysis of Silicate, Carbonate, and Phosphate rocks; Rev. Ed., USGS Bulletin 1401, 1975, pp 54-57.


COMPARISON OF LECO WITH GRAVIMETRIC
(H2O+)
Gravimetric Data
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.5
1.5
2.5
3.5
4.5
Leco Data
Intercept= .039
Slope= .952
R Squared= .99
□ Gravimetric
—— Regression

DETERMINATION OF CARBON AND SULPHUR COMBUSTION/INFRARED ABSORPTION METHOD

Introduction:

In this method, the sample undergoes combustion in a stream of oxygen in a LECO induction furnace. The absorption of infrared (IR) radiation by the CO and CO_2 combustion products are measured by separate detectors with the outputs added electronically to yield a result for total carbon.

The IR absorption of the SO_2 combustion product is measured by a third detector. Results are displayed directly on the instrument as %C and %S.

Sample concentrations are calculated by the instrument using the observed instrument response and the sample weight which is determined by a balance linked to the instrument.

This method determines the total carbon content of a sample (as CO_2) and does not distinguish between carbonate-carbon, organic or graphitic carbon sources. Noncarbonate (graphite) carbon exists in negligible quantities in most rock samples. For this reason $\%CO_2$ is generally considered equal to total carbon. It is convenient to consider this assumption valid, since LECO determinations are substantially faster than other methods (oil displacement, gravimetric, volumetric, carbotrane, etc.). In cases where graphitic carbon is expected to be significant, both total (LECO) and carbonate-carbon (coulometric - Page EA28-1) can be determined and graphitic carbon calculated by difference. (Diamond is rarely encountered).

Safety advisory:

1. Vanadium pentoxide and magnesium perchlorate can cause serious damage to the skin. Exercise caution and wear plastic gloves when handling these materials.
2. The induction furnace generates extreme heat. Always handle crucibles with tongs.

Method:

The method consists of the following techniques:

1. Conversion and separation of the analytes by combustion of the sample.
2. Detection of the analytes by an infrared detector.
3. Calculation of results by reference to standards of known composition.

Apparatus:

- LECO CS-46 Carbon and Sulphur 748-600 System, including:
  - A. Determinator Model 770-200
  - B. Induction Furnace Model 768-100
  - C. EB-25 Electronic Balance
  - D. AWC automatic weight compensation control box
- cylinder of oxygen with 2-stage regulator (2500/35 psi)
- crucibles, including re-usable crucible covers
- tray
- crucible tongs
- quartz combustion tube
- dust traps
- dust filter (10 micron mesh)
- ascarite anhydrone tube
- glass wool
- micro fibre filter tubes

Reagents:

- vanadium pentoxide
- iron chips
- tin pellets
- ascarite, NaOH on asbestos base
- anhydrone, anhydrous, $Mg(ClO_4)_2$

Procedures:

1. Instrument Settings

1.1. Select the following settings for the operation of the CS-46 System:

Power	On
Gas	On
Pump	On
Loop flow	7.5 LPM
Automatic/manual	Auto mode
Data transmit/Inhibit	Inhibit
Function select	Operate
Weight compensator	1000
High carbon blank	Do not adjust
Low carbon blank	Do not adjust
High carbon calibrate	Do not adjust

Low carbon calibrate	Do not adjust
Sulphur blank	Do not adjust
Sulphur calibrate	Do not adjust
Identification code	Do not adjust
Warm-up period	3 hours minimum
Range switch	Do not adjust

1.2. Select the following settings for the operation of the CS-46 Induction Furnace:

Filament voltage	On (glow white)
High voltage	On (glow green)
Oxygen pressure	35 psi

1.3. Select the following settings for the operation of the CS-46 Balance/AWC Control Box:

Power (balance)	On
Auto/Manual switch (box)	Auto

2. Calibration and Sample Analysis

Samples containing 0-2.7% Carbon (0-10% CO_2) and 0-0.8% Sulphur are analyzed by the following steps:

2.1. Turn the oxygen cylinder on and adjust the pressure to 35 psi.

2.2. Add 1 scoop of vanadium pentoxide accelerator to a crucible.

2.3. Place the crucible on the balance pan and press the TARE switch on the AWC control box.

2.4. Add 0.3 g - 0.4 g of reference material to the crucible.

2.5. Press the ENTER switch on the AWC Control Box; the red WEIGHT IN light will activate.

2.6. Add 1 scoop of iron accelerator and 1 tin pellet to the crucible.

2.7. Cover with a lid and place the loaded crucible on the pedestal of the induction furnace.

2.8. Set 'UP/DOWN' switch to 'UP' to begin the analysis cycle; while the sample is being heated, a second sample can be weighed.

2.9. When the CARBON and SULPHUR READ lights glow red, indicating complete analysis, Record the %C and %S readings. If the values deviate from the standard (expected) value, the function switch of the determinator should be rotated to the CALIBRATE position and the calibration dials adjusted to obtain the desired readings.

2.10. Reanalyze the reference material (at least three times) until the readings are consistent with values expected (see QC section).

2.11. Lock the calibration dials and rotate the function switch back to the OPERATE position; the instrument is now ready for sample analysis.

2.12. Samples are analyzed using the steps indicated above.

3. Calculation

Multiply the carbon reading by 3.66 to convert it to equivalent %CO_2.

4. Analysis of Samples with High C or S Concentrations

Samples containing >2.7% C or >0.8% S are analyzed in a similar fashion; less weight (0.1 g or less) of sample is used, the AWC control is not employed and the weights are manually recorded. Results are obtained by dividing the observed results by the sample weight.

5. Instrument Shutdown

5.1. At the end of the analysis remove any remaining crucible from the furnace.

5.2. Turn the O_2 gas supply off and allow any oxygen remaining in the lines to escape.

5.3. Turn the HIGH VOLTAGE and FILAMENT VOLTAGE off.

5.4. Set the PUMP and GAS switches to the off position (down).

5.5. Leave the Determinator and Furnace in this mode for best instrument stability. If the system is expected to be off for an extended period the POWER switch may be turned off.

6. Routine Maintenance

6.1. A system electronics check, as described in the Leco manual (page 17), should be performed daily.

6.2. A leak check, as described in the Leco manual (page 16), should be performed weekly.

6.3. Linear Card Adjustment, (Leco Bulletin 1, 2, 3, 4), is carried out for C, CO_2, or S if erratic readings are obtained during standardization or standardization checks. Typically this happens after two to four weeks of operation.

6.4. The Ascarite and Anhydrone in the oxygen inlet tube should be replaced weekly or whenever it appears moist. The anhydrone in the Bubble Anhydrone tube should be replaced daily - or whenever it appears moist. The combustion tube should be cleaned with a brush every 30 samples; the tube should be inspected from time to time (every 100 samples) for severe pitting and slag build-up. If the tube is deteriorating, it should be replaced.

6.5. The dust-trap on the furnace should be cleaned and the glass wool repacked and conditioned* every 20 samples, or whenever the Loop Pressure reaches 6 psi. It was found that an additional dust-trap filled with $Mg(ClO_4)_2$ was needed, and the glass wool in this additional dust-trap should be replaced at the same time. The 10-micron mesh dust filter should be cleaned daily using an ultrasonic cleaner. About ten minutes is required for this operation.

* Glass Wool Conditioning: The glass wool should be conditioned by heating a crucible with 0.3 g to 0.4 g of a sample containing more than 0.3% sulphur. One scoop of iron chips and one tin pellet are also added to the crucible prior to heating. This operation is only necessary when the glass wool is changed.

Quality Control:

Quality control is carried out by analyzing one in-house reference material every ten samples; blanks are also run.

The optimum range for CO_2 is 0.01-10% and 0.01-0.7% for S.

The instrumental detection limits of C and S are 0.001 and 0.0001% respectively, under ideal conditions. The determination limit for both CO_2 and S is 0.01%.

Precision is estimated at ±5% at the mid-range value for both CO_2 and S (relative).

Productivity:

A technician should be able to complete 30 samples per day.

Additional Notes:

1. The CS-46 system can be calibrated by standards other than reference rocks; synthetic standards can also be prepared to cover the appropriate ranges. Synthetic standards must be calibrated against reference rocks prior to their use as standards.

Bibliography:

Instruction Manual for CS-46 Carbon and Sulphur 748-600 System, LECO Corporation, 1977.

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DETERMINATION OF TOTAL FE VOLUMETRIC (TITRIMETRIC) METHOD

Introduction:

Iron is the fourth most abundant element, comprising about 5 percent of the earths crust. Silicate minerals vary considerably in iron content, and the variation is reflected in the iron content of silicate rocks. Basic rocks may contain 30 to 40 percent iron (calculated as Fe_2O_3), while many acidic rocks contain as little as 1 percent total iron. Ferric iron is frequently associated with aluminum, and ferrous iron with magnesium.

The sulphide mineral pyrite, FeS, and associated minerals of composition $FeSO_4.7H_2O$ in the oxidation zone surrounding pyrite, are common. Iron-containing carbonate minerals are siderite or chalybite $FeCO_3$ and ankerite which is a mixed carbonate or iron, calcium and magnesium.

In this method, the reduction of Fe^{3+} to Fe^{2+} is achieved by stannous chloride in a hot acid (HCl) solution, the excess of which is removed by the addition of mercuric chloride prior to titration. The sample solution is then titrated with standard potassium permanganate solution. The concentration of Fe is calculated on the basis of the net volume after blank subtraction.

This method is used only where the sample matrix makes determination by XRF unsuitable, e.g. when the sulphur content of the rock is too high to allow a fused bead to be prepared for XRF determination.

This method is also applied when the total iron content, expressed as Fe_2O_3, is >15%; above the calibration range of the current XRF method.

This method is also applied for accurate determination where a standard reference material has to be analyzed for certification purposes.

Platinum, vanadium, copper, arsenic, antimony and molybdenum are reduced to a lower valence state like iron, with the addition of stannous chloride and titrated with $KMnO_4$ solution. If present in appreciable amounts, the Fe concentration will appear higher than the true concentration.

Safety advisory:

1. When using HF wear glasses and gloves, and be extremely careful. More information on HF is available in the Geoscience Laboratories' Safety Manual page IV-17.

Method:

The method consists of the following techniques:

1. Sample decomposition by acid digestion and residue fusion (if necessary).
2. Reduction of Fe^{3+} to Fe^{2+} by stannous chloride
3. Titration of the sample solution with standardized potassium permanganate solution
4. Calculation of Fe concentration based on Fe present in the net volume after blank subtraction

Apparatus:

- Teflon beakers, 50 ml
- Glass beakers, 250 ml, 600 ml, 2000 ml
- Vycor brand glass crucible, 30 ml
- Filter paper, Whatman No. 40 (12.5 cm)
- Glass funnels, 75 mm
- Glass burette, 0-50 ml
- Glass wool

Reagents:

- Hydrochloric acid, HCl, 36.5 - 38 %
- Sulphuric acid, H_2SO_4, 96%
- Phosphoric acid, H_3PO_4, 85%
- Stannous chloride, $SnCl_2.2H_2O$
- Mercuric chloride, $HgCl_2$
- Potassium permanganate crystals, $KMnO_4$
- Manganese sulphate, $MnSO_4.4H_2O$
- Potassium pyrosulphate, $K_2S_2O_7$
- Hydrofluoric acid, HF, 48%

Procedures:

1. Reagent preparation

1.1. Stannous chloride, $SnCl_2.2H_2O$ 5% in 10% HCl - Dissolve 10 g $SnCl_2.2H_2O$ in 10 ml of concentrated HCl.

1.1.1. Heat to effect the solution for few minutes if necessary.

1.1.2. Once in solution make to 100 ml with distilled water. The solution should be prepared fresh.

1.2. Mercuric chloride, $HgCl_2$ 5% in H_2O - Dissolve 5 g of $HgCl_2$ in 100 ml of distilled water.

1.3. Zimmermann - Reinhardt reagent - Dissolve 140 g of $MnSO_4.4H_2O$ in 1 liter of distilled water in a 2 liter glass beaker.

1.3.1. Cautiously add 250 ml of concentrated H_2SO_4.

1.3.2. Add 250 ml of 85% phosphoric acid (H_3PO_4).

1.3.3. Dilute to 2 liter with distilled water.

1.4. Potassium permanganate, $KMnO_4$ 0.1N solution - Weigh 32.0 g of potassium permanganate crystals and transfer to approximately 2 liters of distilled water in a 2 liter glass beaker.

1.4.1. Heat to boiling and keep hot for one hour.

1.4.2. Cover and let stand overnight.

1.4.3. Filter the solution through glass wool into a 10 litre dark brown glass bottle.

1.4.4. Add 8 liters of distilled water.

1.4.5. Mix the solution thoroughly, and let stand overnight before standardization.

2. Standardization of $KMnO_4$ - Standardize in triplicate against a National Institute of Standards and Technology (NIST) Reference Material e.g. NIST 29(a) (Fe = 69.54%), or NIST 27(e) (Fe = 66.6%).

2.1. Sample decomposition

2.1.1. Weigh 0.200 g of 29(a) (for example) and transfer to a 50 ml teflon dish.

2.1.2. Add 10 ml of HCl and 10 ml of distilled water.

2.1.3. Heat for a few minutes, make sure most of the sample is in solution.

2.1.4. Add 5 ml of HF.

2.1.5. Evaporate to dryness.

2.1.6. Add 5 ml of concentrated HCl and leave it for 1 or 2 minutes. Then add about 25 ml of distilled water.

2.1.7. Heat well and make sure that the sample is completely dissolved.

2.1.8. If any black gritty particles are noticed, the solution should be filtered, using a Whatman No. 40 filter paper, into a 250 ml beaker. Wash a few times with small portions of hot distilled water. The paper with undissolved particles should be ignited in a Vycor glass crucible (30 ml). Fuse the ignited residue with a small amount of potassium pyrosulphate ($K_2S_2O_7$). Dissolve the fused matter in the crucible by adding distilled water and a small amount of HCl. Heat the crucible on a hot plate until the residue is in solution. Transfer the solution to the original solution in a 250 ml beaker by washing the Vycor crucible a few times with small portions of distilled water.

2.2. Reduction with stannous chloride

2.2.1. Heat to boiling on a hot plate, the complete solution of the sample having a volume of about 50 ml or less.

2.2.2. Add stannous chloride drop by drop until the yellow Fe^{3+} colour disappears. Add one or two drops in excess.

2.2.3. Cover the reduced solution in the beaker with a watch glass and cool by placing in a tray having cold water.

2.2.4. Add rapidly 10 ml of 5% $HgCl_2$ measured in a graduated cylinder.

2.2.5. A small quantity of white precipitate should appear.

2.2.6. If no precipitate, or if the precipitate is grey, the sample should be discarded.

2.3. Titration with $KMnO_4$ (0.1N) solution

2.3.1. After 2 or 3 minutes, transfer the reduced solution quantitatively to a 600 ml beaker, containing 25 ml of Zimmerman - Reinhardt reagent and 300 ml of distilled water.

2.3.2. Titrate immediately with $KMnO_4$ to the first faint pink end point that persists for 15 seconds.

2.3.3. Do not titrate rapidly at any time.

2.3.4. Two blanks should be carried through the procedure.

2.3.5. Correct the volume of $KMnO_4$ for the blank titration.

2.3.6. The standardization should be carried out in triplicate and the average titer taken for the normality.

2.3.7. Calculate the number of milligrams Fe and Fe_2O_3 equivalent to 1 ml of $KMnO_4$.

3. Sample decomposition

3.1. Weigh exactly 0.200 g of sample and transfer to a 50 ml teflon beaker.

3.2. Moisten with distilled water.

3.3. Cover the beaker and add 10 ml of conc. HCl.

3.4. When effervescence has ceased, heat on a hot plate for a few minutes.

3.5. Remove and rinse off the cover into a beaker.

3.6. Add 5 ml of HF (48%).

3.7. Evaporate to dryness.

3.8. Add 5 ml of concentrated HCl and leave it for 1 or 2 minutes. Add 25 ml of distilled water.

3.9. Heat well and ensure that the sample is completely dissolved.

3.10. If any black gritty particles are noticed, the solution should be filtered, using Whatman No. 40 filter paper, into a 250 ml beaker.

3.11. Wash a few times with small portions of hot distilled water. The paper with undissolved particles should be ignited in a Vycor glass crucible (30 ml).

3.12. Fuse the ignited residue a with small amount of potassium pyrosulphate ($K_2S_2O_7$).

3.13. Dissolve the fused matter in the crucible in distilled water and add a small amount of HCl by heating until it is dissolved.

3.14. Transfer the solution to the original solution in the 250 ml beaker by washing the Vycor crucible a few times with small portions of distilled water.

4. Reduction with stannous chloride

4.1. Heat to boiling on a hot plate, the complete solution of the sample having a volume of about 50 ml or less.

4.2. Add stannous chloride drop by drop until the yellow Fe^{3+} colour disappears. Add one or two drops in excess.

4.3. Cover the reduced solution in the beaker with a watch glass and cool by placing in a tray having cold water.

4.4. Add rapidly 10 ml of 5% $HgCl_2$ measured in a graduated cylinder.

4.5. A small quantity of white precipitate should appear, after 2 to 3 minutes.

4.6. If no precipitate or if the precipitate is grey, the sample should be discarded.

5. Titration using $KMnO_4$ (0.1N) solution

5.1. After 2 or 3 minutes, transfer the reduced solution quantitatively to a 600 ml beaker, containing 25 ml of Zimmerman - Reinhardt reagent and 300 ml of distilled water.

5.2. Titrate immediately with $KMnO_4$ to the first faint pink end point that persists for 15 seconds.

5.3. Do not titrate rapidly at any time.

5.4. Two blanks should be carried through the procedure.

5.5. Correct the volume of $KMnO_4$ for the blank titration.

6. Calculation of the results

$$\% Fe = (mg\ Fe/ml\ of\ KMnO_4) \times \left(\frac{\text{ml for } sample - ml \text{ for } blank}{1000}\right) \times \left(\frac{100}{sample\ wt\ (g)}\right)$$

Quality Control:

The determination limit is 0.2% as Fe using a 1.0 g sample.

An estimate of precision, at 95% confidence limit (2σ), at mid-range value (5%) is 0.2% (absolute).

Accuracy is similar to precision for this method.

Productivity:

A technician should be able to complete 15 determinations per day.

Additional Notes:

1. Samples high in sulphur should be roasted first in Vycor brand glass crucibles, 30 ml, in a furnace at 650°C for 3 hours or preferably overnight. Then transfer the powder from the crucible to the teflon beaker. Rinse the crucible with several portions of distilled water and finally with HCl in the teflon beaker.

2. Potassium permanganate is a volumetric oxidizing agent which is used for all ferrous and ferric iron determinations. Its proper preparation and standardization is essential for accurate analysis.

$$5\,Fe^{2+} \longleftrightarrow 5\,Fe^{3+} + 5\,e^-$$

$$5\,e^- + MnO_4^- + 8\,H^+ \longleftrightarrow Mn^{2+} + 4\,H_2O$$

3. The freshly prepared $KMnO_4$ solution is allowed to stand overnight to allow it to react with contaminants such as dust, organic compounds and other oxidizable substances.

4. The $KMnO_4$ solution is filtered to separate MnO_2. The presence of MnO_2 accelerates the decomposition of $KMnO_4$ in solution (autocatalytic process).

$$2MnO_4^- + 4H^+ \longleftrightarrow \underset{(Brown)}{2MnO_2} + 2H_2O + O_2$$

Glass wool is used since filter paper reacts with $KMnO_4$ to yield MnO_2.

5. Stannous chloride is added to reduce Fe^{3+} to Fe^{2+}. A slight excess is added to ensure complete conversion to ferrous iron.

$$Sn^{2+} + 2Fe^{3+} \longleftrightarrow 2Fe^{2+} + Sn^{4+}$$

The excess Sn^{2+} is removed with the addition of mercuric chloride

$$Sn^{2+} + 2HgCl_2 \longleftrightarrow \underset{(White)}{Hg_2Cl_2} + Sn^{4+} + 2Cl^-$$

The insoluble mercurous chloride produced will not consume $KMnO_4$ nor will the mercuric chloride reoxidize Fe^{2+}

Care must be taken not to have a large excess of Sn^{2+} in solution or an alternate reaction with mercuric chloride occurs

$$Sn^{2+}\,(excess) + HgCl_2 \longleftrightarrow \underset{(Black)}{Hg} + Sn^{4+} + 2Cl^-$$

Metallic mercury reacts with permanganate to cause a high result. A proper reduction is indicated by the appearance of a white precipitate. A grey precipitate indicates the presence of mercury and hence discarding of the sample. The total absence of the white precipitate indicates that insufficient amounts of $SnCl_2$ was added.

6. The Zimmerman-Reinhardt reagent is added for the following reasons:

A. The manganous ion inhibits the oxidation of the chloride ion by $KMnO_4$. The chloride oxidation is normally a slow reaction, but Fe^{2+} accelerates it.

$$10Cl^- + 2MnO_4^- + 16H^+ \longleftrightarrow 2Cl_2 + 2Mn^{2+} + 8H_2O$$

B. The phosphoric acid complexes the Fe^{3+} produced in the titration and prevents the intense yellow color of the ferric chloride complexes interfering with the end point. Phosphate ligands provide good oxygen donors for the ferric ion

7. If the addition of $KMnO_4$ is too rapid during titration, some MnO_2 will be produced in addition to the Mn^{2+}. Evidence of this is a faint brown discoloration of the solution. If this occurs, the titration should be stopped until the solution becomes clear. The solution must be free of MnO_2 at the equivalent point.

8. Platinum, vanadium, copper, arsenic, antimony and molybdenum interfere in $KMnO_4$ titration in stannous chloride reduction. Platinum is usually introduced through operations carried out in platinum vessels.

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DETERMINATION OF FERROUS IRON
TITRIMETIC METHOD

Introduction:

Iron is an important industrial commodity. Iron-bearing sedimentary rocks furnish the bulk of industrial iron ore. The main ferruginous groups are: carbonates, silicates, oxides and sulphides.

In addition to its commercial importance, chemical and mineralogical data relating to iron are used in studies researching the origins of rock deposition and metamorphism. (More information about iron is given on page EA14-1).

Since most instrumental analytical techniques do not readily provide information about the oxidation state of constituents it is necessary to employ more classical volumetric techniques. Mossbaur spectroscopy has been used to distinguish iron oxidation states in rocks and minerals but is not suitable for routine analysis.

The rock sample is decomposed by heating with a mixture of sulphuric and hydrofluoric acids in a covered platinum crucible. Most of the iron bearing minerals are decomposed by this procedure forming soluble ferrous and ferric sulphates. The crucible lid and contents are placed in a mixture of boric and sulphuric acids. The solution is titrated against standardized potassium permanganate which oxidizes the ferrous iron to ferric iron.

$$5\,Fe^{2+} \xrightarrow[0.771V]{} 5\,Fe^{3+} + 5e^-$$

$$5\,e^- + MnO_4^- + 8H^+ \xrightarrow[1.51\,V]{} Mn^{2+} + 4H_2O$$

$$MnO_4^- + 5\,Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5\,Fe^{3+} + 4\,H_2O$$

Boric acid is used to remove excess fluoride ion:

$$B(OH)_3 + 2H_2O \longrightarrow B(OH)_4^- + H_3O^+$$

$$H_3O^+ + B(OH)_4^- + 4HF \longleftrightarrow BF_4 + 3H_2O + H_3O^+$$

The method is similar to that described by Goldich. A number of potential interferences are highlighted in the Quality Assurance portion of this method (below).

There are a number of alternative methods in the literature. Wilson's method is based on the reduction of ammonium metavanadate (NH_4VO_3) by ferrous iron.

Unfortunately all methods suffer from various sources of determinate error. The method outlined in this document has the advantage of being relatively rapid and simple.

Safety Advisory:

1. When using HF wear glasses and gloves, and be extremely careful. More information on HF is available in the Geoscience Laboratories' Safety Manual page IV-17.
2. Sulphuric acid, hydrochloric acid, phosphoric acid and potassium permanganate are corrosive substances.
3. Mercuric chloride is toxic.
4. Boric acid can cause skin irritation and may induce an allergic reaction. Avoid contact with any of these materials. Exercise caution when handling these materials. Wear protective clothing and use eye protection.

Method:

The method consists of the following techniques:

1. Sample decomposition using wet chemical procedures.
2. Volumetric analysis using a titrimetric procedure employing potassium permanganate.
3. Calculation of the result.

Apparatus:

- 30 ml platinum crucible with tight fitting lid
- 25 ml polyethylene graduated cylinder
- glass burets, 10 ml and 50 ml
- glass beakers, 600 ml, 1 liter, 2 liter
- florence flask, 1 liter
- tongs for platinum crucible
- teflon beakers, 100 ml and 250 ml
- glass wool
- 10 liter container for standardized potassium permanganate

Reagents:

- boric acid crystals
- concentrated sulphuric acid
- concentrated hydrofluoric acid
- potassium permanganate crystals
- NBS 29A Iron Ore Standard, 69.54% Fe
- stannous chloride, $SnCl_2.2H_2O$
- hydrochloric acid, 6.8 M
- phosphoric acid, 15 M
- manganese sulphate, $MnSO_4.4H_2O$
- mercuric chloride, $HgCl_2$

Procedures:

1. Reagent Preparation

1.1. Saturated boric acid - Prepare a saturated solution by adding approximately 900 ml of (recently boiled and cooled to room temperature) distilled water to 50 g of boric acid crystals in a flask. It is convenient to employ three, one liter beakers for the purpose of providing sufficient water (see Additional Notes, below).

1.2. Decomposition Solution - Prepare a solution of (recently boiled and cooled to room temperature) distilled water, sulphuric and hydrofluoric acids in a 1:1:1 volume ratio using the teflon beaker. Approximately one hundred ml, total volume, is generally sufficient for this purpose.

1.3. N/10 (0.1 N) Standard Potassium Permanganate - Weigh 32.0 g of potassium permanganate crystals.

1.3.1. Transfer approximately 2 liters of recently boiled and cooled distilled water to a 2 liter beaker.

1.3.2. Add the potassium permanganate crystals to the contents of the 2 liter beaker.

1.3.3. Heat to boiling and keep hot for one hour.

1.3.4. Cover and let stand overnight.

1.3.5. Filter the solution through glass wool into the 10 liter permanganate container.

1.3.6. Add 8 liters of (recently boiled and cooled) distilled water and mix the solution thoroughly.

1.3.7. Allow to stand overnight before standardizing.

1.4. Stannous Chloride - Dissolve 37.5 g of iron-free stannous chloride in 250 ml of 6 N hydrochloric acid. This solution should be freshly prepared.

1.5. Mercuric Chloride - Dissolve 50 g of mercuric chloride in 1 liter of distilled water.

1.6. Zimmerman Reinhardt Reagent - Dissolve 140 g of manganese sulphate in 1 liter of distilled water.

1.6.1. Cautiously add, with stirring, 250 ml of concentrated sulphuric acid.

1.6.2. Cautiously add, with stirring, 250 ml of phosphoric acid.

1.6.3. Dilute to 2 liters with (boiled and cooled) distilled water.

2. Standardization of Potassium Permanganate Solution

2.1.1. Weigh 0.200 g of NBS 29a Iron Ore and place in a 250 ml teflon beaker. A blank should also be carried through the procedure.

2.1.2. Add 10 ml of 6 N hydrochloric acid and 10 ml of HF.

2.1.3. Place on hotplate and evapourate to dryness.

2.1.4. Add 10 ml concentrated HCl.

2.1.5. Add 50 ml distilled water.

2.1.6. Place on hotplate and heat to dissolve. Heat the solution nearly to boiling.

2.1.7. Add stannous chloride solution drop by drop until the yellow Fe^{3+} colour disappears. Add one drop in excess.

2.1.8. Cool to room temperature.

2.1.9. Transfer 25 ml of Zimmerman Reinhardt reagent to a clean 600 ml beaker. Add 300 ml (boiled and cooled) distilled water.

2.1.10. Load buret with unstandardized potassium permanganate solution.

2.1.11. Rapidly add 10 ml of the mercuric chloride solution. A small quantity of white precipitate should appear. If no precipitate is observed or if the precipitate is grey the sample should be discarded.

2.1.12. After 2-3 minutes, transfer the reduced solution quantitatively to the 600ml beaker containing 25ml of Zimmerman Reinhardt reagent and 300ml of distilled water.

2.1.13. Titrate immediately with $KMnO_4$ to the first faint pink end point that persists for 15 seconds. Do not titrate rapidly at any time.

2.1.14. Repeat steps 2.1.2. through 2.1.13. with the blank solution.

2.1.15. Correct the volume of $KMnO_4$ for the blank titration by subtracting the volume of permanganate reagent required to titrate the blank from that required to titrate the NBS standard.

2.1.16. Repeat steps 2.1.1. through 2.1.13. two more times.

2.1.17. Calculate the average titre.

2.1.18. Calculate the number of grams of Fe equivalent to 1 ml of $KMnO_4$:

$$\frac{g\ Fe}{ml\ KMnO_4} = Fe\ equivalent = Fe\ Eq$$

$$Fe\ Eq = \frac{(Weight\ NBS\ Std) x (Mol\ Fraction\ NBS)}{ml\ KMnO_4}$$

e.g.,
Weight NBS: 0.20 g
Mol Fraction NBS: 0.6954
ml $KMnO_4$: 22.50

$$Fe\ Eq = \frac{0.20 \ x \ 0.6954}{22.5} = 0.006181\ g$$

3. Decomposition of Samples

3.1.1. Weigh 0.500 g aliquot of homogeneous powdered sample and transfer to a 30 ml platinum crucible.

3.1.2. Moisten the sample with a small portion of (boiled and cooled) distilled water.

3.1.3. Add 15 ml of the decomposition solution and immediately cover the crucible with a tight fitting lid.

3.1.4. Place the crucible on a hot plate and bring the contents to a boil.

3.1.5. Adjust the temperature of the hot plate so that violent boiling does not occur.

3.1.6. Transfer 200 ml (boiled and cooled) distilled water to a clean 600 ml beaker.

3.1.7. Add 50 ml of saturated boric acid solution.

3.1.8. Add 5 ml sulphuric acid.

3.1.9. After 10 minutes, grasp the crucible around its centre with the tongs, hold the lid in place with a stirring rod, and transfer the crucible and lid into the 600 ml beaker containing 200 ml boiled distilled water, 50 ml of saturated boric acid and 5 ml of sulphuric acid.

4. Measurement of Ferrous Iron

4.1.1. Fill the burette with standardized $KMnO_4$ solution.

4.1.2. Immediately following dissolution, use the glass buret and titrate the contents of the 600 ml beaker with 1/10N (0.1 N) potassium permanganate. Stir thoroughly throughout the titration to a faint pink end point that persists for several seconds.

4.1.3. Calculate the %Fe from the titre:

$$\%\ Fe = \frac{ml\ KMnO_4\ x\ Fe\ Eq}{g\ Sample} x\ 100\ \%$$

e.g.,
ml $KMnO_4$: 5.21
Fe Eq: 0.006181g
g Sample: 0.223

$$\%\ Fe = \frac{5.21\ x\ 0.006181\ g}{0.223\ g} x\ 100\% = 14.4\ \%\ Fe$$

4.1.4. Calculate the %FeO, and $\%Fe_2O_3$ from the %Fe:

$Fe \rightarrow FeO$ 71.8/55.8 = 1.286
%FeO = %Fe x 1.286
$Fe \rightarrow Fe_2O_3$ 159.7/(2 x 55.8) = 1.430
$\%Fe_2O_3$ = %Fe x 1.430

Quality Control:

The quality of the analysis is controlled by running a standard reference material (MRB-11 7.37% Fe) and a blank. The blank should yield results of less than the reporting increment (0.1%) and the SRM should be within ±8% (relative), (i.e. MRB-11 6.78% - 7.96%) with within run precision of better than 2%.

The optimum range for analysis is 0.1% to 10%.

The minimum readable volume of the titre should be not more than 0.025 ml. The determination limit is 0.10% FeO with a 0.5 g aliquot.

Precision, at the 95% confidence level (2σ), is 0.2% (relative) at the mid-range value of 5%.

There are a number of sources of determinate error:

1. Iron can be introduced as a contaminant during the rock crushing operation where steel crushers are used.
2. Also, significant ferrous iron can be air oxidized while the sample is being ground since the surface exposed to the atmosphere is greatly increased. Studies carried out by Fitton and Gill showed that the measured ferrous iron content of a basalt rock dropped from 6.8% to 6.0% after only four minutes of grinding. They recommend no more than thirty seconds of grinding for rocks that are to be analyzed for ferrous iron. They do not comment on the effect of incomplete grinding on the accuracy or precision of the method.

Langmhyr et al have reported difficulties with incomplete sample dissolution. Some iron-bearing minerals are refractory and even prolonged boiling will not decompose them. Tourmaline $H_4NaFe_3Al_6O_{31}$, Staurolite $Fe(OH)_2(Al_2SiO_5)_2$, Ilmenite $FeO.TiO_2$, Magnetite $FeO.Fe_2O_3$ are examples. FeS_2 is particularly difficult to dissolve. Development of a method employing steel clad teflon lined bombs may yield a method that would open out these minerals.

The presence of sulphide minerals at levels greater than 8% in the sample may introduce determinate error and a resulting high bias in the results. Sulphur can reduce some of the Fe^{3+}.

If accurate results are required it may be necessary to develop a method where the samples are ground in an inert atmosphere using tungsten carbide or other suitable grinding material.

Productivity:

A technician should be able to complete 30 samples per day.

Additional Notes:

1. Efficiency is improved if samples are run in sets of two. Two samples are weighed and queued for analysis. During the ten minute analysis time for these samples, the next two samples can be weighed and, if required, V_2O_5 may be added.
2. Always keep plenty of hot distilled water on hand. This water is used for making the saturated boric acid solution (50 ml per sample). It is convenient to use three separate one litre beakers for this purpose. The first is boiled and removed from the hotplate. While it is cooled, the second is placed on the hotplate to boil. When the first is cool, 50 g of boric acid are added. When the second has boiled it is removed from the hotplate and allowed to cool. The third follows the second through this process. When the first solution is used the first beaker follows the third and the cycle continues.
3. In the presence of HF, ferrous iron may oxidize to ferric iron. The boric acid removes fluoride ions, forming BF_6^{2-}. The sequestering of fluoride ions prevents oxidation of the iron. The boric acid also aids in obtaining a lasting end point.
4. Pyrites are not dissolved by this procedure.

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DETERMINATION OF TRACE ELEMENTS (T3)
X-RAY FLUORESCENCE SPECTROSCOPY

Introduction:

The Philips PW1400 XRF spectrometer system is used for the quantitative determination of the trace elements and Th, Rb, Sr, Y, Zr, and Nb. This combination of elements is referred to as the Trace 3 (T3) package. Cs, Ga, Ta, Ce, La and Nd can be determined as "additions".

Rb, Sr: These elements are found in many minerals including micas, amphiboles, pyroxenes, feldspars and less common minerals such as apatite and carbonate minerals. One isotope of Rb (87) decays over a geologically useful time interval to 87Sr, thus the relative abundance ratio of this pair of isotopes can be used to date rock units.

Zr, Nb, Y, Rb, Ce, Ta: These elements, found in rock-forming minerals and accessory minerals, are used extensively to characterize the tectonic setting of basalts and granites. The processes that control the formation of magma at different regions within the earth also control the relative abundances of these elements, thus resulting in characteristic elemental signatures in different areas.

Th, Cs, Ga: These elements substitute for more abundant elements in rock or minerals (e.g. Th follows Zr and U, Cs follows Rb and Li, and Ga substitutes for Al). Comparison of trace element/major element abundances can be used to track the interplay between formation or alteration process in rock units. Ga/Al ratios are used to understand unusual granites related to ore deposits; Cs is used to characterize fluid/magma/crystal interaction. Th is used either as a petrogenetic discriminator or XRF determinations can pre-screen samples high in Zr and Th that will be used for geochronology.

Ta, Cs, Y, Zr, Nb, Ta, La, Nd: These elements are usually only found at ppb-ppm levels in rock samples. Several of the world's major economic producers of these elements are located in Canada (Tanco, Manitoba, and Thor Lake, NWT.).

Safety advisory:

The main sources of danger from this method are from X-radiation and from electric shock. Fire danger exists, as well as potential for eye damage during the sample preparation. There is some potential danger associated with the movement of bottled compressed gas. For more details refer to the Safety Advisory listed on page EA6-6.

Method:

The method consists of the following techniques:

1. Matrix modification by pressing samples into pellets
2. Irradiation and measurement of characteristic X-ray fluorescence using a sequential, wavelength-dispersive X-ray spectrometer
3. Calculation of final results using calibration curves stored in the instrument's computer

Samples are prepared as pellets in a similar manner to that described in method EA6, "Majors - XRF". General theoretical considerations are presented in Volume I of this manual.

Apparatus:

- Balance capable of weighing 1-20 g ± 0.001 g
- Ring press and die (40 mm)
- Aluminum "former sleeve"
- Plexiglass plunger
- Boric acid measuring vial (25 ml)
- Spex pellet press (Model 3624B)

Reagents:

- Boric acid (granular)
- Polyvinyl alcohol (2% w/v in distilled water)

Procedures:

1. Preparation of Pressed Powder Pellets for XRF Determination of Trace Elements in Rock Powder

1.1.1. Wearing gloves, weigh 5.0 g (0.1 g) of -200 mesh rock pulp into a 7 dram snap-cap plastic vial.

1.1.2. Add three drops of polyvinyl alcohol solution (to serve as a binder) and blend into the powder by stirring with a nickel spatula.

1.1.3. Transfer the sample to the 40 mm die to which an aluminum "former sleeve" has been added.

1.1.4. Pack the contents with a plexiglass plunger to form a compact puck.

1.1.5. Remove the sleeve and plunger and add the boric acid powder, placing it on top of the sample. A measuring vial in the boric acid container indicates the amount to be added.

1.1.6. Complete the assembly of the die and form the pellet by application of 15 tons pressure for 15 seconds using the pellet press.

1.1.7. Removed the pellet from the die and label it with a felt-tipped marker on the boric-acid side.

1.1.8. Leave the pellet face-down on a cellulose wipe for 24 hours to allow the binder to dry.

A well-made pellet should have no cracks, an even surface and the rock powder should be centered within the outer ring of boric acid. If a pellet is considered unsuitable, a new one is made from a fresh subsample of rock pulp.

It is important to keep the dies clean. Boric acid and rock powder can build up on the surfaces and contaminate subsequent samples. A thorough cleaning with a cellulose wipe after each pellet is removed will generally suffice. Methanol should be used on the wipe to give a more thorough cleaning. The surface in contact with the rock powder must be treated with care. It can become pitted and must then be polished by gently rubbing the surface with a fine abrasive moistened with methanol.

Application and release of pressure on the die-press should be even and slow. The die must be placed centrally and must be level. Failure to do so can result in uneven loading and mechanical failure.

2. Nondestructive Analysis

The use of the Philips PW1400 X-ray Fluorescence Spectrometer System is described in the Section 'Majors - XRF', page EA6-1.

3. Calculation of Final Results

All necessary calculations are performed automatically by the system computer.

Quality Control:

It is important to distinguish between short-term (batch) precision and long-term (multi-year) precision. Short-term precision on jobs and daily assays is monitored via duplicate analyses of 10% of all samples submitted. These duplicates are subjected to identical preparation and analytical procedures. International reference materials (IRM) are used to monitor short-term precision and accuracy. One IRM similar in composition to the sample group being analysed is inserted into group of six samples (for both jobs and assays). These replicate and IRM data are assessed before the data for geological material are released.

The Ontario Geological Survey carries out many multi-year projects. The analytical data used in the resulting report may come from rocks collected and submitted for analysis over a period of several years. For the geological interpretations to be significant, they must be based on a realistic evaluation of the long-term precision.

One of the Laboratories' blind-duplicate quality control programs involves the insertion of one subsample of three in-house reference materials (a granite, a basalt, and a syenite), in the routine analytical work on a monthly basis. The precision data from this program are used to derive the Laboratories' advertised analytical capabilities. The stringency of the test allows us to have confidence that the figures we quote are realistic, even when applied to multi-year projects. The rock-powder samples are introduced 'blind' into the routine workflow and are subject to no special procedures, as often happens when an analyst is aware that QC samples are being run.

Productivity:

A technician should be able to complete 40 samples per day.

Bibliography:

Health and Welfare Canada, Health Protection Branch, Bureau of Radiation and Medical Devices, 775 Brookfield Rd., Ottawa, Ontario, K1A 1C1.

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Abbey, S., 1983, Studies in "Standard Samples of Silicate Rocks and Minerals", GSC Paper 83-15.

Govindaraju, K., 1989, 1989 Compilation of Working Values and Sample Descriptions for 272 Geostandards, Geostandards Newsletter, Vol. 13, pp 1-113.

Nockolds, S., Average Chemical Composition of Some Igneous Rocks, Bull. Geol. Soc. America, Vol. 65.

Potts, P.J., Handbook of Silicate Rock Analysis, Blackie, Scotland, 1987, 622 pages.

Determination Limits and Precision for Trace Element Analysis

Element	Determination Limit (ppm)	Optimum Range (ppm)	Precision (ppm)*
Nb	3	3-3000	5
Rb	5	5-1000	5
Sr	5	5-1000	5
Th	10	10-5000	10
Y	5	5-1000	10
Zr	5	5-1000	10
Additions			
Ce	35	35-5000	40
Cs	3	3-3000	3
Ga	5	5-1000	5
La	35	35-1000	40
Nd	20	20-5000	20
Ta	10	10-5000	10

* Precision is quoted (in ppm) as the 95 percent confidence limit (2σ) for values at 10X the determination limit.

APPENDIX A
TRACE ELEMENT DETERMINATIONS - MEASUREMENT PROGRAMS

Measurement Program for the Determination of T3 Elements

For this program, preliminary corrections (found in the RC set) include background correction factors and interference factors which are determined independently.

Corrections and Calibration

Background corrections: A fused disc of pure silica is used to evaluate background correction parameters. These factors are determined from three background points in the scan across the analyte 2-theta angles, i.e., the Y offset (Y+) for Sr, Y, Zr, Rb, U and Nb; Th+ for Th, and Pb+ for Pb. In order to avoid negative intensities, only 95% of the background correction factor is used in the correction.

Interference corrections: Preliminary correction for interferences are introduced for U on Rb and for Rb on U. Factors obtained from running samples with high interferent and negligible analyte are listed under L2 in the RC table above. As these L2 factors are the fraction of the total counts of the interferent element which must be subtracted from the total counts of the interfered element, without regard to background correction, only partial correction is made at this stage of the data reduction. Mass Absorption (MA) correction is made by ratioing all intensities to the Compton line intensity. Final correction is made using the alpha influence factors.

Calibration: The standard reference materials used in the calibration include NIML, SY3, MicaFe, MAN, GH, GA and MRG1. These represent a variety of silicate matrices and cover a wide range of concentrations of analytes.

Zr	up to	1.1%	(NIML)
Y	up to	0.07%	(SY3)
Sr	up to	0.46%	(NIML)
Rb	up to	0.36%	(MAN)
Th	up to	0.099%	(SY3)
U	up to	0.066%	(SY3)
Pb	up to	0.013%	(SY3)
Nb	up to	0.96%	(NIML)

The Measurement program (in OTHER) used for the Trace 3 package is MP5 and the parameters are listed below:

MP5

MASK : 1
ABS : YE

CHAN	PT	PC	CHAN	PT	PC
Rh	20	0E0	Nb	100	0E0
Zr	100	0E0	Y	100	0E0
Y+	40	0E0	Sr	100	0E0
U	100	0E0	Rb	100	0E0
Th	100	0E0	Th+	40	0E0
Pb	100	0E0	Pb+	40	0E0

This measurement program is also used for the determination of individual elements in this group (given the extent of mutual interference and alpha correction factors).

The Link program LP5 specifies the rate corrections and shows that all analyte channels are ratioed to the Compton scatter peak (RH) channel (listed as internal standard) for mass absorption corrections.

LPNR=5 NRCH= 8 CPNR= 5 MODLST= 0 MBNR= 0 LLNR = 0 OPTION = 0

INT1 = RH

ELMNT	Zr	Y	Sr	U	Rb	Th	Pb	Nb
RC	1	2	3	4	5	6	7	8

Accepted values (Abbey, 1983; Govindaraju, 1989) of element concentrations (in ppm) used in the calibrations are listed below:

	Zr	Y	Sr	U	Rb	Th	Pb	Nb
MicaFe	800	25	5	60	2200	150	13	270
NIM-L	11000	25	4600	14	190	65	43	960
GA	150	21	310	4	175	17	30	10
SY3	320	740	306	650	208	990	130	130
MAN	27	1	84	12	3600	1	29	175
MRG-1	105	16	260	<1	8	1	10	20
GH	150	70	10	18	390	90	45	85
BEN	270	30	1350	2.4	47	11	4	100

Calibration curves obtained from the DJ (De Jongh) model are linear. Coefficients D, E and alpha values are stored in CP 5 and are listed below:

ELM	ND	NC	D	E	CEL	ALPHA	CEL	ALPHA
Pb	3	0	0.00636	3.77756				
Th	3	1	0.00068	3.04205	Rb	-9.54918		
Rb	3	0	-0.00376	1.18923				
U	3	1	0.00036	2.93207	Rb	-19.07030		
Sr	3	0	0.00839	0.91437				
Y	3	1	0.02234	1.10890	Rb	-28.09171		
Nb	3	2	-0.00257	0.89649	Zr	-30.95473	Th	-40.7827
Zr	3	2	0.02175	0.77185	Sr	-35.05055	Th	-0.84639

Agreement with expected and calculated values is generally good. For example, in an initial calibration of Zr, the following agreements were obtained (where Exp. = expected Zr values based on Govindaraju, 1989; Calc^1 = Zr determination based on calibration over full concentration range, Calc^2 = Zr determination based on limited concentration range, i.e. excluding NIM-L).

Standard	Exp. (ppm)	Calc^1 (ppm)	Calc^2 (ppm)
MicaFe	800	753	810
NIM-L	11100	11080	N/A
GA	150	133	139
SY3	320	330	320
MAN	27	29	36
MRG-1	105	106	113
GH	150	119	132
BEN	270	348	271

The agreement between Exp. and Calc^2 indicates calibration over more limited ranges is preferable. The disagreement between Exp. and Calc^1 could be assigned to various factors including:

- wide range of calibration with assumption of linearity over the total range, from 27 to 11,000 ppm;
- questionable accepted values;
- limited data for calculation of alphas;
- applicability of the utilization of the Rh Compton line for the mass absorption correction

The applicability of the Rh Compton line can be assessed using the program on page EA16-9, which calculates the mass absorption based on background counts (MA(B)), Compton counts (MA(C)) and major elements (MA(Majors)). Analysis of calibration intensity data results in the following data (based on the mass absorption of SY3 for Sr being 12.6).

Reference	MA(B)	MA(C)	MA(Maj.)
MAN	11.2	7.22	7.81
NIM-L	10.0	16.5	12.8
Mica Fe	13.3	21.1	19.7
GH	11.7	7.77	9.40
MRG-1	13.7	18.2	17.6
QTZ	13.2	8.22	7.34
SY2	13.0	11.9	12.0
G1	12.0	8.11	9.33
DRN	13.5	12.6	12.8
GA	12.1	8.50	9.58
Mica Mg	13.4	13.3	13.1

In all cases, the Compton-computed value in the previous table (MA(C)) is closest to the MA from the major-element composition (MA(Major)). This indicates the validity for using the Compton line in the calculation of the corrected counts for calibration.

NIM-L is not a typical rock sample, because it contains percent level Zr and very high Sr, an interferent. The above calibration is carried out over a high range of concentrations. If a smaller range is used (i.e., NIM-L included), the agreements are indicated in Calc^2. Thus the NIM-L Zr determination is over-corrected for the extremely high level of Sr found in this sample (4600 ppm).

This example shows that the standards used in a calibration are often not representative of "normal" silicate rocks. In unusual cases, attention should be paid to the overall composition of the sample, especially unusually high levels of trace elements. XRF scans are often used to detect the latter. The agreement between expected and calculated values for other Trace 3 elements is generally good.

Measurement Program for the Determination of Gallium

Gallium is determined as a separate measurement program, MP3, stored in DB/PB OTHER. Channel conditions are highlighted below:

```
Rh  Kα  NO  F  S  1  1  75  25  50  40  18.300
Ga  Kα  NO  F  S  1  1  75  25  50  40  38.845  .46
Ta  Lβ  NO  F  S  1  1  75  25  50  40  38.465  .30
```

Tantalum (Ta Lβ line at 2-theta 38.450°) is not expected to be a significant interferent on the Ga analyte line (Kα 38.834°) in the vast majority of rock samples. Because VSN is used as the highest concentration standard for the calibration of Ga, and as it contains 900 ppm Ta, the potential interference is accounted for in the program.

Measuring program parameters are listed below:

```
MP3

MASK      :   1
ABS       :   YE

CHAN      PT     PC
Rh        20     0E0
Ta-       20     0E0
Ta        40     0E0
Ga        40     0E0
Ga+       20     0E0
```

Analysis of a quartz pellet over the four measured positions, Ta-, Ta, Ga and Ga+, indicated background correction factors:

Correction for Ta = 0.9260 Ta-
Correction for Ga = 1.1150 Ga+

Analysis of a high level tantalum standard (Ta1540) indicated an interference contribution at the Ga position of 0.111

Rate correction summary:

```
 9  0  Ta-   0.9260            0.0000    0.0000    0.0000
10  0  Ga+   1.1150    TA      0.1111    0.0000    0.0000
```

Link Program 3:

```
LP3

LPNR = 3  NRCH = 2  CPNR = 3  MODLST = 0  MRBR=0  LLNR=0
OPTION =     0
INT1     =   RH
ELEMENT      Ta      Ga
RC           9       10
INTR         RH
```

(The ratioing to the Compton line gave a good mass absorption correction for the Ga line, but not for the Ta line.)

Calibration factors were determined using the standards listed below. Expected and calculated values obtained in the original calibration are listed below. Calibration coefficient and alpha correction values (Ta on Ga and Ga on Ta) are stored in CP3.

GALLIUM

	Literature ppm	Observed ppm
NIM-S	11	96
SY3	26	29
MAN	59	51
VSN	400	401

Additional standards run as a program check indicate the following values:

NIM-L	54	58
GH	23	17
BEN	17	19
MRG-1	18	20
SY2	28	29

Counting statistics on the background of the VSN sample were used to calculate the detection limit at 3-4 ppm. Determination limit was established at 5 ppm in the rock sample.

TANTALUM

	Literature	Observed
NIM-S	?	-25
Mica Fe	34	38
SY3	?	21
MAN	310	328
VSN	900	870

Tantalum agreement is poor at low levels, however approximation at higher levels is adequate for correction purposes. This program should not be used to determine Ta values, instead use that outlined overleaf.

Measurement program for the Determination of Tantalum

XRF is used to determine tantalum in rocks to a determination of limit of 10 ppm.

Analytical parameters are found in PB/DB GEORHO, with measurement and link programs MP8 and LP8 and calculation parameters in CP8.

Channel conditions for the elements are:

ELEMENT	FLT	COL	DET	XTL	ORD	UPL	LWL	KV	MA	ANGLE	+OFFS	-OFFS
Rh Kα	NO	F	S	1	1	75	25	50	40	18.300		
Ta^1 Kα	NO	F	S	1	1	65	35	75	40	44.375		
Ta^2 Kα	NO	F	S	1	1	65	35	75	40	45.520		
Cu Kα	NO	F	S	1	1	65	35	75	40	44.995		

The two tantalum channels correspond to peak (TA1) and background positions (TA2).

The tantalum line lies between the copper Kα and nickel Kβ lines. These two elements rarely occur in tantalum-bearing rocks; however, they may be present in components of the X-ray spectrometer and are assumed to interfere with the Ta line. The resolving power of the PW1400 X-ray spectrometer is high enough to clearly separate the Ta and Ni lines, so copper is the only serious interferent in the determination.

Rate corrections used include: (1) the subtraction of Cu intensity due to the spectrometer (obtained from a wavelength scan of a quartz blank), and (2) background correction.

MP8

MASK : 1
ABS : YE

CHAN	PT	PC
Rh	20	0E0
Ta^1	100	0E0
Cu	40	0E0
Ta^2	40	0E0

In the development of the link program, it was observed that the best fit was obtained using Compton scatter MA correction for the Cu and background MA correction for the tantalum line.

LP8

LPNR=8 NRCH=2 CPNR=8 MODLST=0 MBNR=0 LLNR= 0
OPTION= 0
INT1= RH INT2= TA2

ELMNT	Ta^1	Cu
RC	14	15
INTR	Ta^2	Rh

Rate corrections observed (and stored in the RC table under GEORHO) are listed:

NR	BKGR	CHL1	L1	CHL2	L2	CHL3	L3	CHL4	L4
14	0	Ta^2	1.0126		0.0000		0.0000		0.0000
15	40	Ta^2	1.0000		0.0000		0.0000		0.0000

There are no natural reference materials which have a high certified value for Ta. The synthetic glass VSN is used in the calibration of both Cu and Ta (concentration values: Ta = 900? ppm, Cu = 800 ppm).

Calibration standards used include:

TANTALUM

SRM	Literature ppm	Observed ppm
VSN	900	900
MAN	310	310
Mica Fe	35	36

COPPER

SRM	Literature ppm	Observed ppm
VSN	800	801
MAN	140	132
Mica Fe	4	<5
NIM-S	19	30

The calculation parameter file indicates that tantalum is calibrated with an alpha correction for the copper interference.

As stated above, determination limit for tantalum was established to be 10 ppm in the rock sample.

Measurment program for the Determination of Ce, La and Nd

The rare earth elements Ce, La and Nd are generally determined in conjunction with the T4 package using ICP Mass Spectrometry. In certain cases, where the concentrations of these elements are expected to be high, XRF can be used for the determinations.

There are two cerium lines in this wavelength region, the Lα 79.01° and the Lβ at 71.70° (2-theta). The Lα line has a barium interference (Ba Lβ 79.26°) and is avoided in favour of the Ce Lβ line.

MP13, LP13 and CP13 in the OTHER file are used for the determination.

Channel conditions and rate correction parameters are outlined below:

ELEMENT	FLT	COL	DET	XTL	ORD	UPL	LWL	KV	MA	ANGLE	+OFFS	-OFFS
Ce LB	NO	F	F	1	1	70	30	65	30	71.600		0.70
Nd LA	NO	F	F	1	1	60	25	65	30	72.121	0.80	
La LA	NO	F	F	1	1	70	25	65	30	82.865		1.00

Background correction factors are obtained from the intensities observed at the peak and offset positions (Ce-, Nd+, La-). In the original procedure reported in earlier manuals (for the PW1540), slope in the background was taken into account by calculating the background correction factor as

$$Bf = I(peak)/(B1 + B2)$$

To simplify calculations, and as this program is intended only for relatively high concentrations of these elements, background correction factors are obtained from single points, e.g.,

$$Bf(Ce) = I(Ce)/I(Ce-)$$

No correction is made for mass absorbance. This region of the spectrum does not lend itself to the method of Feather and Willis (background) nor is the Compton scatter ratio meaningful. If the major-element data are available, MA corrections may be applied. However for most samples, MA variations are expected to be minimal and good values should be obtained without correction.

Interference factors may be calculated and inserted in the RC table. The program uses alpha factors exclusively for inter-element correction.

NR	BKGR	CHL1	L1	CHL2	L2	CHL3	L3	CHL4	L4
11	0	Ce-	.9200		0.0000		0.0000		0.0000
12	0	Nd+	1.1105		0.0000		0.0000		0.0000
13	0	La-	1.0000		0.0000		0.0000		0.0000

```
MP13

MASK     :   1
ABS      :   YE

CHAN     PT     PC
Ce-      50     0E0
Ce       100    0E0
Nd       100    0E0
Nd+      50     0E0
La-      50     0E0
La       100    0E0

LPNR= 13  NRCH= 3  CPNR= 13   MOPDLST= 0   MBNR= 0  LLNR= 0
OPTION = 0
ELMNT    Ce      Nd      La
RC       11      12      13
```

Best fit was obtained for Ce and La without alpha corrections. Nd uses an alpha correction for Ce.

Using a 50 second counting time at the background position, counting statistics indicated relatively poor detection limits for Ce, La and Nd. Determination limits were established as 35, 35 and 20 ppm respectively.

Measurement Program for the Determination of Cesium

The chromium X-ray tube is favoured for the determination of cesium in rock samples. Channel conditions stored in DB/PB GEORHO are listed below.

ELEMENT	FLT	COL	DET	XTL	ORD	UPL	LWL	KV	MA	ANGLE	+OFFS	-OFFS
Cs Lα	NO	F	F	1	1	80	15	75	40	91.865	2.00	

Measurement program and link program are stored under GEORHO as MP21 and LP21 with calibration coefficient information in CP21.

Background correction is applied as indicated below:

NR	BKGR	CHL1	L1	CHL2	L2	CHL3	L3	CHL4	L4
16	0	Cs+	1.1165		0.0000		0.0000		0.0000

Calibration without MA correction results in a good fit with a wide range of standards:

CESIUM

SRM	Literature ppm	Observed ppm
VSN	900	900
Mica Fe	200	205
GA	6	6
Mica Mg	55	59
GXR-3	200	178
NBS1633A	11	14

Determination limit is estimated to be 3 ppm.

APPENDIX B

MASS ABSORPTION CALCULATION PROGRAM FOR APPLE IIE

```
10    D$ =  CHR$ (4)
20    FF$ =  CHR$ (12)
30    DIM A$(100),M1(100),M2(100),M3(100)B1(100),B2(100)
100   NS$ = " ":NC$ = " "
200   HOME
205   PRINT : PRINT "THIS PROGRAM CALCULATES MASS ABSORPTION"
210   PRINT "COEFFICIENTS USING....": PRINT "BACKGROUND COUNTS":
      PRINT"COMPTON SCATTER COUNTS": PRINT " MAJOR ELEMENT COMPOSITION"
215   PRINT : PRINT : PRINT "DO YOU WANT TO USE BKG. COUNTS...Y/N..";:
      INPUT A$
220   PRINT : PRINT "DO YOU WANT TO USE COMPTON COUNTS..Y/N..";: INPUT B$
230   PRINT : PRINT "DO YOU WANT TO USE MAJOR ELEMENTS..Y/N..";: INPUT C$
240   HOME
250   IF A$ = "Y" THEN 259
255   GOTO 300
```

For calculation on background....

```
259   HOME : PRINT : PRINT "FOR BACKGROUND...": PRINT : PRINT
260   INPUT "NAME OF MA REFERENCE ";NS$
265   INPUT "MA VALUE FOR REFERENCE ";MA
270   INPUT "BKG COUNTS FOR REFERENCE ";BC
280   KB = MA * BC
```

For calculation on Compton....

```
300   IF B$ = "Y" THEN 309
305   GOTO 350
309   HOME : PRINT "FOR COMPTON...": PRINT : PRINT
```

Initialization of 100 entries....

```
350   HOME
360   FOR I = 1 TO 100
365   NA$(I) = " ":M1(I) = 0:M2(I) = 0:M3(I) = 0:B1(I) = 0:B2(I) = 0
370   NEXT  I
310   INPUT "NAME OF MA REFERENCE ";NC$
315   INPUT "MA VALUE OF REFERENCE ";MN
320   INPUT "COMPTON COUNTS FOR REF.  ";CC
325   KC = MN * CC
```

Data Entry ....

```
400   I=0
405   I=I+1
410   PRINT : PRINT : INPUT "NAME OF SAMPLE..";NA$(I)
415   PRINT
420   IF A$ = "N" THEN 430
421   PRINT : INPUT "BKG COUNTS ";B1(I)
425   M1(I) = KB / B1(I)
426   M1(I) =  INT (M1(I) * 10000) / 10000
```

```
430   IF B$ = "N" THEN 440
431   PRINT : INPUT "COMPTON COUNTS  ";B2(I)
435   M2(I) = KC / B2(I)
436   M2(I) =  INT (M2(I) * 10000) / 10000
440   IF C$ = "N" THEN 750
```

For calculation using the major elements ...

```
450   HOME
451   T = 0
455   PRINT "ENTER THE FOLLOWING CONCENTRATIONS AS": PRINT "% OXIDE"
460   PRINT : PRINT
```

For each element, the operator inputs the oxide concentration as a percentage, which is then converted to a weight fraction. The MA contribution is calculated from both the analyte and oxygen components. For example in lines 465-471, the fraction Si in SiO2 is 0.4675 and the fraction of oxygen is (1-0.4675 = 0.5325). The MA values for Si and O at the Sr K-alpha line are 12.8 and 2.6 respectively; T = the accumulated total MA.

```
465   INPUT "SIO2  ";SI
470   SI = SI / 100
471   T = T + SI * .4675 * 12.8 + SI * .5325 * 2.6
475   PRINT : INPUT "AL2O3 ";AL
476   AL = AL / 100
477   T = T + AL * .5291 * 10.3 + AL * .4709 * 2.6
480   PRINT : INPUT "TOTAL FE2O3 ";FE
481   FE = FE / 100
482   T = T + FE * .6994 * 66.8 + FE * .3006 * 2.6
485   PRINT : INPUT "MGO   ";MG
486   MG = MG / 100
487   T = T + MG * .6032 * 8.1 + MG * .3968 * 2.6
490   PRINT : INPUT "CAO    ";CA
491   CA = CA / 100
492   T = T + CA * .7147 * 33.7 + CA * .2853 * 2.6
495   PRINT : INPUT "NA2O  ";NN
496   NN = NN / 100
497   T = T + NN * .7919 * 6.3 + NN * .2081 * 2.6
500   PRINT : INPUT "K2O    ";KK
501   KK = KK / 100
502   T = T + KK * .8302 * 29.5 + KK * .1698 * 2.6
505   PRINT : INPUT "TIO2  ";TI
506   TI = TI / 100
507   T = T + TI * .5995 * 43.3 + TI * .4005 * 2.6
510   PRINT : INPUT "P2O5  ";PP
511   PP = PP / 100
512   T = T + PP * .4365 * 15.6 + PP * .5635 * 2.6
515   PRINT : INPUT "MNO   ";MM
516   MM = MM / 100
517   T = T + MM * .7744 * 60.5 + MM * .2256 * 2.6
520   PRINT : INPUT "CO2    ";CC
521   CC = CC / 100
522   T = T + CC * .2720 * .9 + CC * .7280 * 2.6
525   PRINT : INPUT "H2O  ";HH
526   T = (HH / 100) * .8889 * 2.6 + T
530   PRINT : INPUT "SULFUR ";SS
535   SS = SS / 100
536   T = T + SS * 18.7
```

```
540   HOME
545   PRINT "DO YOU WANT TO INCLUDE BA AND F?"
550   PRINT : PRINT "...Y/N...";: INPUT R$
555   IF R$ = "N" THEN 600
560   PRINT : PRINT : INPUT "PPM BA  ";BA
565   BA = BA / 1000000
566   T = T + BA * 76.3
570   PRINT : PRINT : INPUT "PPM F  ";FF
571   FF = FF / 1000000
572   T = T + FF * 3.4
600   T =  INT (T * 10000) / 10000
605   M3(I) = T
```

Another sample.....

```
750   HOME : PRINT : PRINT "DO YOU WANT ANOTHER SAMPLE?": PRINT
      "....Y/N..";:     INPUT R$
755   IF R$ = "Y" THEN 405
800   M = I
```

Printing sequence ...

```
810   PRINT D$;"PR#2"
820   PRINT : PRINT "MASS ABSORBANCE CALCULATIONS"
830   PRINT : PRINT
840   IF A$ = "Y" THEN  PRINT "BKG. REFERENCE = ";NS$;"     MA = ";MA
850   IF B$ = "Y" THEN  PRINT "COMPTON REF. = ";NC$;"     MA = ";MN
860   IF C$ = "Y" THEN  PRINT "MAJOR ELEMENT CALCULATIONS INCLUDED"
870   PRINT : PRINT : PRINT
880   PRINT  CHR$ (27)"D" CHR$ (20) CHR$ (40) CHR$ (60) CHR$ (0)
890   PRINT  CHR$ (9); CHR$ (3)
900   G$ =  CHR$ (9)
910   PRINT "SAMPLE";G$"MA(BKG)";G$"MA(COMP)";G$"MA (MAJORS)"
920   PRINT : PRINT
930   FOR I = 1 TO M
940   IF A$ = "Y" AND B$ = "Y" AND C$ = "Y" THEN 960
950   GOTO 970
960   PRINT NA$(I);G$M1(I);G$M2(I);G$M3(I)
970   IF A$ = "Y" AND B$ = "Y" AND C$ = "N" THEN 990
980   GOTO 1000
990   PRINT NA$(I);G$M1(I);G$M2(I);G$"  "
1000  IF A$ = "N" AND B$ = "Y" AND C$ = "Y" THEN 1020
1010  GOTO 1030
1020  PRINT NA$(I);G$"  ";G$M2(I);G$M3(I)
1030  IF A$ = "Y" AND B$ = "N" AND C$ = "Y" THEN 1050
1040  GOTO 1060
1050  PRINT NA$(I);G$M1(I);G$"  ";G$M3(I)
1060  IF A$ = "Y" AND B$ = "N" AND C$ = "N" THEN 1080
1070  GOTO 1090
1080  PRINT NA$(I);G$M1(I);G$"  ";G$"  "
1090  IF A$ = "N" AND B$ = "Y" AND C$ = "N" THEN 1110
1100  GOTO 1120
1110  PRINT NA$(I);G$"  ";G$M2(I);G$"  "
1120  IF A$ = "N" AND B$ = "N" AND C$ = "Y" THEN 1140
1130  GOTO 1150
1140  PRINT NA$(I);G$"  ";G$"  ";G$M3(I)
```

```
1150 NEXT I
1155 PRINT FF$
1160 PRINT  CHR$ (27)"@"
1170 PRINT D$;"PR#0"
1500 END
```

APPENDIX C
MASS ABSORBANCE VALUES FOR SELECTED SILICATE S.R.MS

SRM	MA(Sr-Kα)	SR	MMA(Sr-Kα)
MRB-7	14.5	SY-2	12.0
MRB-8	8.7	SY-3	12.6
MRB-9	9.0	MRG-1	17.5
MRB-10	9.5		
MRB-11	10.9	GA	9.5
		GH	8.7
NIM-G	9.0	VSN	12.7
NIM-D	13.8	UBN	9.9
NIM-L	13.2	Mica Fe	19.4
NIM-S	10.7	DTN	7.5
NIM-P	13.5	DRN	12.7
NIM-N	12.8	FKN	9.5
		Mica Mg	12.8
G-2	9.5	GSN	10.0
W-1	13.8	BXN16.2	
GSP-1	10.4	BR 15.3	
BCR-1	14.5		
SGR-1	8.2	QUARTZ	7.4
SDC-1	11.1		
RGM-1	9.1	ANG	11.3
STM-1	10.3	MAN	7.8
BHVO-1	14.5	BEN	8.2
SCO-1	10.1		
MAG-1	11.3		
QLO-1	10.4		
G-1	8.8		

APPENDIX D
MA FACTORS (SR K- α WAVELENGTH)

Li	.1	Rb	23.6	Lu	145.4
Be	.2	Sr	25.4	Hf	151.3
B	.5	Y	27.4	Ta	156.9
C	.9	Zr	29.5	W	163.5
N	1.5	Nb	31.7	Re	169.2
O	2.6	Mo	33.8	Os	175.1
F	3.4	Tc	36.3	Ir	181.4
Ne	4.7	Ru	38.8	Pt	186.7
Na	6.3	Rh	41.4	Au	164.7
Mg	8.1	Pd	44.0	Hg	122.2
Al	10.3	Ag	47.0	Tl	125.8
Si	12.8	Cd	49.6	Pb	130.2
P	15.6	In	52.7	Bi	134.0
S	18.7	Sn	55.6	Po	138.2
Cl	22.0	Sb	58.9	At	61.9
Ar	25.6	Te	61.9	Rn	64.6
K	29.5	I	65.7	Fr	67.6
Ca	33.7	Xe	68.8	Ra	20.7
Sc	38.3	Cs	72.4	Ac	73.9
Ti	43.3	Ba	76.3	Th	77.5
V	48.6	La	80.2	Pa	81.2
Cr	54.3	Ce	84.2	U	85.5
Mn	60.5	Pr	88.0	Np	90.1
Fe	66.8	Nd	92.7	Pu	96.0
Co	73.7	Pm	97.3		
Ni	81.0	Sm	100.8		
Cu	88.6	Eu	105.5		
Zn	96.5	Gd	110.4		
Ga	104.8	Tb	115.1		
Ge	113.5	Dy	120.0		
As	122.8	Ho	124.3		
Se	132.7	Er	129.7		
Br	143.6	Tm	135.7		
KR	21.8	Yb	140.5		

(Reference: Henrich's Tables)

APPENDIX E
XRF DETECTION LIMIT CALCULATION

```
10    D$ =  CHR$ (4)
15    PRINT : PRINT "TURN ON PRINTER"
20    PRINT D$;"PR#2"
30    PRINT : PRINT "DETECTION LIMIT = COUNTS XRF"
35    PRINT : PRINT
36    INPUT "ELEMENT NAME ";EL$
40    INPUT "BACKGROUND COUNTS ";B
50    INPUT "PEAK COUNTS = ";P
55    N = P - B
60    PRINT "P-B = ";N
65    INPUT "CONCENTRATION OF ELEMENT ";C
70    M = (P - B) / C
80    PRINT "CONCENTRATION FACTOR = ";M
85    INPUT "COUNT TIME AT BKG ";TB
90    PRINT : PRINT
91    DL = (3 / M) *  SQR (B / TB)
92    DL =  INT (DL * 100) / 100
100   PRINT "D.L. = (3/M)(SQRT B/TB) = ";DL
110   PRINT : PRINT
120   PRINT : PRINT "MORE....Y/N"
130   INPUT R$
140   IF R$ = "Y" THEN 35
149   PRINT D$;"PR#0"
150   END
```

APPENDIX F
RATE CORRECTION PARAMETERS

Trace-element determinations are divided into several groups or packages and divided within the software into several measurement programs. Measurement programs under file OTHER use a common rate correction file, RC, which is listed below:

NR	BKGR	CHL1	L1	CHL2	L2	CHL3	L3	CHL4	L4
1	0	Y+	1.3021		0.0000		0.0000		0.0000
2	0	Y+	1.0855	Rb	.2600		0.0000		0.0000
3	0	Y+	.9090		0.0000		0.0000		0.0000
4	0	Y+	.8262		0.0000		0.0000		0.0000
5	0	Y+	.7967	U	.1400		0.0000		0.0000
6	0	Th+	1.2203		0.0000		0.0000		0.0000
7	0	Pb+	1.1717		0.0000		0.0000		0.0000
8	0	Y+	1.5614		0.0000		0.0000		0.0000
9	0	Ta-	.9260		0.0000		0.0000		0.0000
10	0	Ga+	1.1150	Ta	.1111		0.0000		0.0000
11	0	Ce-	.9200		0.0000		0.0000		0.0000
12	0	Nd+	1.1105		0.0000		0.0000		0.0000
13	0	La-	1.0000		0.0000		0.0000		0.0000
14	0	Nb-	.9307		0.0000		0.0000		0.0000
16	0	Cs+	1.1165		0.0000		0.0000		0.0000
17		Nb-	.9000		0.0000		0.0000		0.0000

DETERMINATION OF TRACE ELEMENTS
(Co, Cr, Cu, Ni, Pb, Zn, Ba, Li, Ag, Cd, Mn, Fe)
ATOMIC ABSORPTION SPECTROMETRY

Introduction:

The trace elements Co, Cr, Cu, Ni, Pb, Zn, Ba, Li, Mn, and Fe can be determined in all geological materials by atomic absorption spectrometry. Although manganese and iron are not considered trace, they are determined in samples, such as soils and tills, known to contain less Mn and Fe than rocks. Silver and cadmium are determined on samples digested without HCl acid.

The average trace element content of various igneous rocks is listed in Table AAS1. Considerable variations in these values may occur, especially with samples which include specific minor accessory minerals which contain these elements as major components.

The following is a list of minerals containing these trace elements. The minerals are significant, not only because they can increase the normal expected abundance in a rock, but because many of them are resistant to mineral acid attack and require fusion techniques to provide a complete dissolution. Ore grade materials may contain high percentages of these minerals thus producing analytical results in the percent range.

COBALT

Cobaltite	CoAsS
Skutterudite	$(Co,Ni)As_3$
Smaltite	*
Erythrite (cobalt bloom)	$(Co,Ni)_3(AsO_4)_2$

* an arsenic deficient variety of skutterudite

CHROMIUM

Chromite	$FeCr_2O_4$

Cr in rocks and soils is generally present as chromic oxide.

COPPER

Native metal	Cu
Chalcopyrite	$CuFeS_2$
Bornite	Cu_5FeS_4
Cuprite	Cu_2O
Malachite	Cu_2CO_3

Cu is in most sulphide ores. There are 600 Cu minerals.

NICKEL

Braggite	(Pt,Pd,Ni)S
Millerite	NiS
Pentlandite	$(Fe,Ni)_9S_8$
Pyrrhotite	
Kupfernickel	As mineral

Ontario has the world's greatest abundance of nickel.

LEAD

Galena	PbS
Cerussite	$PbCO_3$
Wulfenite	$PbMoO_4$
Anglesite	$PbSO_4$

Inorganic salts of lead are relatively insoluble.

ZINC

Sphalerite	ZnS
Smithsonite	$ZnCO_3$

BARIUM

Barite	$BaSO_4$
Witherite	$BaCO_3$

Barium in solution is precipitated by sulphate and carbonate ions.

LITHIUM

Spodumene	$LiAlSiO_6$
Petalite	$(Li,Na)(Al,Si_4O_{10})$
Amblygonite	Li,Al PO_4 (F,OH)
Hectorite	complex silicate *

* can contain up to 1% Li_2O
Li compounds are very soluble.

MANGANESE

Pyrolusite	MnO_2
Alabandite	MnS
Rhodocrosite	$MnCO_3$

SILVER

Native metal	Ag
Argentite	Ag_2S
Acanthite	AgS

TABLE AAS1. TRACE ELEMENT CONTENT (PPM) IN IGNEOUS ROCKS

Element	Ultrabasic	Gabbro	Intermediate	Granite	Pegmatite
Co	100	50	15	3	1
Cr	3000	200	50	25	30
Cu	50	100	50	15	5
Ni	1000	120	40	10	3
Pb	0.3	3	6	20	?
Zn	50	100	70	50	200?
Ba	20	200	1600	950	700?
Li	3	10	20	40	60
Mn	1000	1400	1400	400	400
Ag(ppb)	60	110	60	40	?
Cd			0.2		

Most Ag compounds are relatively insoluble. Silver is associated with Pb-Zn ores.

CADMIUM

Greenockite	Cd_2SO_4

Cadmium is associated with ZnS ores.

Safety advisory:

1. Exercise extreme care when using any acids and fluxes required for sample dissolution. Their use should only be attempted after the appropriate **MSDS** sheets have been read and the safe handling and first aid procedures understood. Acids should only be handled in a fume hood designated for their use and proper protective equipment worn. Proper ventilation is required when handling fluxes which create a dust control problem.

2. Before operating an atomic absorption spectrophotometer, ensure that the proper instructions found in the manufacturer's operator's manual are understood. Preliminary safety checks are noted in the section of this manual outlining the operation of an atomic absorption spectrophotometer.

3. Cylinders of compressed gas used as fuel and oxidant for flame atomic absorption spectrometry must be securely fastened and have the proper regulator. Ensure that the system has no leaks and the gas hoses are in good condition. Review the section on compressed gases found in the Safety Manual for the Geoscience Laboratories.

Apparatus:

- Atomic Absorption Spectrometer

A. Varian AA 775

B. Varian AA-5 (IM-6 update)
  - Strip Recorder - Varian Model 9176 or Linear Model 1200
  - Pipettes - 5, 10, 20, 25, 50 ml
  - Volumetric flasks - 50, 100, 200, 250, 500, 1000, 2000 ml
  - Acid dispensers - Socorex Model 511 (10 ml)
  - Various sized glass beakers

Reagents:

- Nitric acid, HNO_3, 69% (w/w)
- Stock Standard Solutions (1000 ppm)
    - A. Custom Mixed Standard containing Co, Cu, Ni, Pb, Zn, Mn, Fe, Ag.
    - B. Chromium
    - C. Lithium
    - D. Barium
    - E. Cadmium
- Potassium Chloride, KCl
- Lanthanum Oxide, La_2O_3, suitable for flame enhancement in atomic absorption spectrometry.

Method:

The method consists of the following techniques:

1. Sample decomposition by either acid digestion or fusion with a flux

2. Measurment of analyte signal by atomic absorption spectrometry

3. Calculation of results based on calibration curves produced from synthetic samples.

Procedures:

1. Reagent preparation

1.1. Lanthanum/Potassium Reagent for Barium Determination (6000 ppm La^{3+} / 6000 ppm K^+) - Carefully add 200 ml of nitric acid to 14.07 g of lanthanum oxide placed in a 600 ml covered glass beaker. CAUTION: Reaction is vigorous and generates heat.

1.2. To a 2 liter volumetric flask add 22.89 g of KCl and dissolve with 200 ml of distilled water.

1.3. Transfer the lanthanum solution when cool to the volumetric flask and dilute to 2 liters with distilled water.

2. Preparation of Calibration Working Standards

2.1. Working standards are prepared by dilution of the custom mixed stock solution, with 10% nitric acid. Typical concentrations of analytes in working standards range from 0.5 to 8 ppm.

2.2. Lithium standards: Add 20 ml of 10,000 ppm K^+ for every 100 ml of working standard prepared. Final concentration of K^+ is 2000 ppm. Working standards are prepared by serial dilution of the stock lithium solution with 10% nitric acid.

2.3. Chromium standards: Add 10 ml of 10,000 ppm K^+ for every 100 ml of working standard prepared. Final concentration of K^+ is 1000 ppm. Working standards are prepared by serial dilution of the stock chromium solution with 10% nitric acid.

2.4. Barium standards: Add 50 ml of 6000 ppm La^{3+}/K^+ for every 100 ml of working standard prepared. Final concentration of La^{3+}/K^+ is 3000 ppm. Working standards are prepared by serial dilution of the stock barium solution with 10% nitric acid.

3. Sample Decomposition

3.1. Samples are digested with mineral acid using either HNO_3-$HClO_4$-HF (Procedure 1), or HCl-HF-HNO_3 (Procedure 3), or HNO_3-HF (Procedure 5). Details are found in the section on sample dissolution by acid attack.

3.2. Samples are decomposed by fusion using lithium metaborate (Procedure 1) or sodium peroxide (Procedure 2). Details are found in the section on sample dissolution by fusion.

3.3. Preparation of samples for Barium determination - Dilute 1 part of sample solution with 1 part of 6000 ppm La^{3+}/K^+ prior to determination by atomic absorption spectrometry.

4. Measurement of Analyte Concentration by Atomic Absorption Spectrometry

A Varian AA775 is used for the determination of trace elements in solution. See "Operation of the Atomic Absorption Spectrophotometer - Varian AA775" on page EA4-1 in this manual for the steps required to obtain a concentration for each element of interest.

Consult the information sheets at the end of this section for the instrument parameters and necessary details to perform the determination of each trace element.

Samples with concentration of the element greater than the upper limit of its calibration curve are to be diluted to the appropriate level for remeasurement.

5. Calculation of results

Calibrate the instrument with the working standard solutions according to the instructions in the operator's manual. The spectrometer is constantly adjusted to distilled water zero, thus the number obtained from the digital readout is in concentration units, usually ppm. This reading is converted to a result for the sample by the following:

$$R = (C - B) \times DF$$

where

R = analyte concentration in the sample

C = concentration measured in solution

B = reagent blank concentration

DF = dilution factor from the preparation step

For a barium determination, a strip recorder is used to obtain a trace of the absorbance of the calibration standards and the sample. Peak heights are measured and concentration in solution for the sample is determined by simple ratio with the peak heights of the calibration standards. The above equation is used to calculate the result for the sample.

6. Reporting

All results are reported on appropriate Trace Element Analysis Forms. See the manual "Processing of Whole Rock Chemical Data - Ontario Geological Survey" for all details.

Normally the trace element forms will be computer generated and complete with sample numbers, geologist's name and job number. If these are not available the appropriate identifying data and correctly sequenced sample numbers will be entered by the Laboratories staff doing the analysis. Correctly sequenced sample numbers refer to the order as written in the Geoscience Laboratories Job Sheet. There are five column spaces for each analytical result. The first four are for the numerical value of the determined concentration, the fifth for the unit of concentration. Concentration may be entered as percent (P), ppm (M), or ppb (B). The use of a decimal point is allowed in any of the first four columns. A blank in the unit column is assumed to be ppm (M). Amounts less than the detection limit will be recorded as the detection limit preceded by a "minus" sign (e.g. -5 indicates a value below the detection limit of 5). N.D. and are not allowed.

The Trace Form 1 is used to report the T1 elements Co, Cr, Cu, Ni, Pb, Zn, Ba, Li, and Ag. The Trace Form 5 is used to report Cd.

The Trace Form 7 is used to report "major" and "minor" elements (Mn, Fe) when they occur at trace levels.

Assay samples are reported on Form 1117 - Assay Work and Report Form.

Quality control and Additional notes:

Accuracy: In the absence of interfences, accuracy may approach precision but is dependent on the quality of the standard solution used. Blind duplicate and SRM quality contol data confirm that this method can remain under good analytical control indefinitely. This note applies to all of the following information sheets.

Cobalt Co

STANDARD SOLUTIONS

Use 100 ppm solution prepared from 1000 ppm mixed custom stock solution to prepare working standards of 0.5, 1.0, 2.0, and 4.0 ppm.

INSTRUMENT PARAMETERS

Lamp Current (ma)	7.0
Wavelength (nm)	240.7
Spectral Band Pass (nm)	0.2
Background Correction	ON
Flame Description	

Air-acetylene, oxidizing, fuel lean, blue

WORKING CONDITIONS

Sensitivity
1 ppm Co solution reads 0.145 absorbance
Calibration
Set 1.00 ppm to read 0.50
Working range
0.5 to 4.0 ppm

INTERFERENCES

Minimal interferences have been observed with the air-acetylene flame.

A cobalt response can be depressed in the presence of excess nickel (1500 ppm). Either dilute the sample, if possible, or matrix match the sample and standards.

NOTES

1. To reduce signal noise, the gain is reduced by setting working standards to one-half values during calibration. The subsequent readout for samples must be multiplied by 2 before reporting to obtain the correct concentration value.

ANALYTICAL CAPABILITIES

Determination Limit (ppm) 5

Precision, at the 95% confidence limit (2σ), at 10X determination limit (50 ppm) is 5 ppm (absolute).

Chromium Cr

STANDARD SOLUTIONS

Use 100 ppm solution prepared from 1000 ppm stock Cr solution to prepare 1.0, 2.0, 4.0 and 8.0 ppm working standards. Add 10 ml of 10,000 ppm K$^+$ for every 100 ml of working standard prepared. 1 ml = 1000 ppm K$^+$

INSTRUMENT PARAMETERS

Lamp Current (ma)	5.0
Wavelength (nm)	357.9
Spectral Band Pass (nm)	0.2
Background Correction	OFF

Flame Description
  Nitrous oxide-acetylene
  Fuel rich, red cone

WORKING CONDITIONS

Sensitivity
  1 ppm Cr solution reads 0.090 absorbance
Calibration
  Set 1 ppm to read 0.50
Working range
  1.0 to 8.0 ppm

INTERFERENCES

The nitrous oxide-acetylene flame overcomes most supressions observed with an air-acetylene flame.

Ionization suppression is eliminated by addition of 1000 ppm K$^+$ to the working standards. Most rock samples have sufficient alkali concentration to eliminate the need for addition of K$^+$ to the sample solution.

NOTES

1. To reduce signal noise, the gain is reduced by setting working standards to one-half values during calibration. The subsequent readout for samples must be multiplied by 2 before reporting to obtain the correct concentration value.

ANALYTICAL CAPABILITIES

Determination Limit (ppm) 10

Precision, at 95% confidence limit (2σ), at 10X determination limit (100 ppm) is 20 ppm (absolute).

Copper Cu

STANDARD SOLUTIONS

Use 100 ppm solution prepared from 1000 ppm mixed custom stock solution to prepare working standards of 0.5, 1.0, 2.0 and 4.0 ppm.

INSTRUMENT PARAMETERS

Lamp Current (ma)	3.5
Wavelength (nm)	324.8
Spectral Band Pass (nm)	0.5
Background Correction	OFF

Flame Description
  Air-acetylene, oxidizing, fuel lean, blue

WORKING CONDITIONS

Sensitivity
  1 ppm Cu solution reads 0.200 absorbance
Calibration
  Set 1.00 ppm to read 1.00
Working range
  0.5 to 4.0 ppm

INTERFERENCES

Few interferences with air-acetylene flame.

One percent Fe in solution, i.e., 50% Fe in the sample, can cause a 10% suppression.

High Zn/Cu ratios can cause some suppression of the Cu signal. Use a leaner air-acetylene flame to minimize this effect.

ANALYTICAL CAPABILITIES

Determination Limit (ppm) 5

Precision, at the 95% confidence limit (2σ), at 10X determination limit (50 ppm) is 4 ppm (absolute).

Nickel Ni

STANDARD SOLUTIONS

Use 100 ppm solution prepared from 1000 ppm mixed custom stock solution to prepare working standards of 0.5, 1.0, 2.0 and 4.0 ppm.

INSTRUMENT PARAMETERS

Lamp Current (ma)	5.0
Wavelength (nm)	232.0
Spectral Band Pass (nm)	0.2
Background Correction	ON
Flame Description	
Air-acetylene, oxidizing, fuel lean, blue	

WORKING CONDITIONS

Sensitivity
1 ppm Ni solution reads 0.120 absorbance.
Calibration
Set 1.00 ppm to read 0.50
Working range
0.5 to 4.0 ppm

INTERFERENCES

Non-atomic species in the air-acetylene flame absorb strongly at 232.0 nm; background correction is necessary.

NOTES

1. To reduce signal noise, the gain is reduced by setting working standards to one-half values during calibration. To obtain the correct concentration value for the samples, the readout must be multiplied by 2 before reporting the result.
2. A non-resonant line for Ni exists at 231.6 nm. Make sure the correct wavelength is chosen when the instrument is being "peaked".
3. Calibrations with 232.0 nm are usually very curved because of a non-resonant line of Ni at 232.14 nm. This is of particular importance with samples of low Ni content-use a 0.5 ppm Ni calibration standard.

ANALYTICAL CAPABILITIES

Determination Limit (ppm) 5

Precision, at the 95% confidence limit (2σ), at 10X determination limit (50 ppm) is 6 ppm (absolute).

Lead Pb

STANDARD SOLUTIONS

Use 100 ppm solution prepared from 1000 ppm mixed custom stock solution to prepare working standards of 0.5, 1.0, 2.0 and 4.0 ppm.

INSTRUMENT PARAMETERS

Lamp Current (ma)	5.0
Wavelength (nm)	217.0
Spectral Band Pass (nm)	1.0
Background Correction	ON
Flame Description	
Air-acetylene, oxidizing, fuel lean, blue	

WORKING CONDITIONS

Sensitivity
1 ppm Pb solution reads 0.060 absorbance.
Calibration
Set 1.00 ppm to read 0.50
Working range
0.5 to 4.0 ppm

INTERFERENCES

Few serious interferences have been reported.

NOTES

1. The 283.3 nm line is sometimes preferred because of its better signal to noise ratio than the 217.0 nm line, although the sensitivity is one-half.
2. To reduce signal noise, the gain is reduced by setting working standards to one-half values during calibration. To obtain the correct concentration value for the samples, the readout must be multiplied by 2 before reporting.

ANALYTICAL CAPABILITIES

Determination Limit (ppm) 10

Precision, at the 95% confidence limit (2σ), at 10X determination limit (100 ppm) is 8 ppm (absolute).

Zinc Zn

STANDARD SOLUTIONS

Use 100 ppm solution prepared from 1000 ppm mixed custom stock solution to prepare working standards of 0.5, 1.0, 2.0 and 4.0 ppm.

INSTRUMENT PARAMETERS

Lamp Current (ma)	5.0
Wavelength (nm)	213.9
Spectral Band Pass (nm)	1.0
Background Correction	ON
Flame Description Air-acetylene, oxidizing, fuel lean, blue	

WORKING CONDITIONS

Sensitivity
1 ppm Zn solution reads 0.325 absorbance
Calibration
Set 1.00 ppm to read 1.00
Working range
0.5 to 3.0 ppm

INTERFERENCES

Non-atomic species in the air-acetylene flame absorb strongly at 213.7 nm. Background correction is necessary.

NOTES

1. Calibration curve will bend at ends. For samples with low Zn content calibration with a low standard (0.5 ppm) is necessary.

2. Dilute solutions containing more than 3 ppm Zn. Linearity drops off sharply in this range. Attempts to calibrate with standards 3 ppm require excessive curve correction and cause the calibration to be unstable.

ANALYTICAL CAPABILITIES

Determination Limit (ppm) 10

Precision, at the 95% confidence limit (2σ), at 10X determination limit (100 ppm) is 10 ppm (absolute).

Barium Ba

STANDARD SOLUTIONS

Use 100 ppm solution prepared from 1000 ppm stock Ba solution to prepare 1.0, 2.0, 4.0 and 8.0 ppm working standards. Add 50 ml of 6000 ppm La^{3+}/K^{+} solution for every 100 ml of working standard prepared. 1 ml = 3000 ppm La^{3+}/K^{+}

INSTRUMENT PARAMETERS

Lamp Current (ma)	10
Wavelength (nm)	553.6
Spectral Band Pass (nm)	1.0
AA5 (100)	
Background Correction	OFF
Flame Description Nitrous oxide-acetylene Fuel lean, small red cone	

WORKING CONDITIONS

Use a strip recorder to trace absorbance readings.

For Varian Model 9176 set chart speed at 1 cm/min, mV/FS at 5, 1 ppm Ba signal for 3".

Working range
1.0 to 2.0 ppm - 5 mV/FS
2.0 to 4.0 ppm - 10 mV/FS
4.0 to 8.0 ppm - 20 mV/FS

INTERFERENCES

Ionization in the nitrous oxide-acetylene flame is suppressed with the addition of K^{+} to samples, standards and blanks.

Stable compound interference from phosphate, silicate, aluminate, etc. is minimized in a nitrous oxide-acetylene flame and/or by addition of La^{3+}.

NOTES

1. In the region of 553.6 nm strong emissions from Ba and the nitrous oxide-acetylene flame contribute to the noise of the absorbance signal. A strip recorder is used to record the signal. The noise may also be reduced by increasing the lamp current and thereby decreasing the PM voltage.

2. Run calibration standards frequently to ensure no loss in sensitivity. If this occurs, check fuel flow, burner clogging, or loss of peak alignment.

3. Dilute samples outside of largest calibration range BEFORE adding "buffer" solution.

ANALYTICAL CAPABILITIES

Determination Limit (ppm) 10

Precision, at the 95% confidence limit (2σ), at 10X determination limit (100 ppm) is 16 ppm (absolute).

Lithium Li

STANDARD SOLUTIONS

Use 100 ppm solution prepared from 1000 ppm stock Li solution to prepare 0.5, 1.0, 2.0 and 4.0 ppm working standards. Add 20 ml of 10,000 ppm K^+ for every 100 ml of working standard prepared. 1 ml = 2000 ppm K^+

INSTRUMENT PARAMETERS

Flame Emission - Single Beam

Wavelength (nm)	670.8
Spectral Band Pass (nm)	0.2
Background Correction	OFF

Flame Description
Nitrous oxide-acetylene

Fuel lean, small red cone

WORKING CONDITIONS

While aspirating a 2 ppm Li solution, set absorbance to read approximately 0.750.

Calibration
Set 1.00 ppm to read 1.00
Working range
0.5 to 4.0 ppm

INTERFERENCES

Ionization in a nitrous oxide-acetylene flame is overcome with the addition of 2000 ppm K^+.

NOTES

1. Most rock samples have sufficient concentration of easily ionizable substances to eliminate the need for addition of K^+ to the sample solution.

2. The air-acetylene flame in the emission mode generates excessive signal to noise levels.

ANALYTICAL CAPABILITIES

Determination Limit (ppm) 3

Precision, at the 95% confidence limit (2σ), at 10X determination limit (30 ppm) is 3 ppm (absolute).

Manganese Mn

STANDARD SOLUTIONS

Use 100 ppm solution prepared from 1000 ppm mixed custom stock solution to prepare working standards of 0.5, 1.0, 2.0 and 4.0 ppm.

INSTRUMENT PARAMETERS

Lamp Current (ma)	5.0
Wavelength (nm)	279.5
Spectral Band Pass (nm)	0.2
Background Correction	OFF
Flame Description	

Air-acetylene, oxidizing, fuel lean, blue

WORKING CONDITIONS

Sensitivity
1 ppm Mn solution reads 0.300 absorbance
Calibration
Set 1.00 ppm to read 1.00
Working range
0.5 to 4.0 ppm

INTERFERENCES

The presence of phosphate, perchlorate, iron, nickel and cobalt will depress the Mn absorbance when a reducing air-acetylene flame is used. USE an oxidizing flame.

Silicon depresses the signal and is overcome by incorporation of 0.2% $CaCl_2$ in samples and standards.

NOTES

1. The presence of silica in samples fused with lithium metaborate may cause a depression in the Mn absorbance if insufficient Ca is present in the sample. Use certified reference materials as calibration standards. See "Major Elements Determined by Flame Atomic Absorption" in this manual.

2. The closely spaced triplet formed by the three strongest absorption lines of Mn may not be resolved with all monochromators.

3. Most soils and sediments require a 1:10 dilution to be made on the solution prepared by acid digestion.

ANALYTICAL CAPABILITIES

Determination Limit (ppm) 5

Precision, at the 95% confidence limit (2σ), at 10X determination limit (50 ppm) is 10 ppm (absolute).

Iron **Fe**

STANDARD SOLUTIONS

Use 100 ppm solution prepared from 1000 ppm mixed custom stock solution to prepare working standards of 0.5, 1.0, 2.0 and 4.0 ppm.

INSTRUMENT PARAMETERS

Lamp Current (ma)	5.0
Wavelength (nm)	248.3
Spectral Band Pass (nm)	0.2
Background Correction	OFF

Flame Description
Air-acetylene, oxidizing, fuel lean, blue

WORKING CONDITIONS

Sensitivity
1 ppm Fe solution reads 0.145 absorbance
Calibration
Set 1.00 ppm to read 0.50
Working range
0.5 to 4.0 ppm

INTERFERENCES

A reduction in sensitivity has been observed when iron is determined in the presence of nitric acid and nickel. This effect is minimized by using a very lean flame.

All interferences can be removed with the use of a nitrous oxide-acetylene flame.

NOTES

1. To reduce signal noise, the gain is reduced by setting working standards to one-half values during calibration. To obtain the correct concentration value for the samples, the readout must be multiplied by 2 before reporting the result.
2. Most soils and sediments require a 1:100 dilution to be made on the solution prepared by acid digestion. This has the added effect of reducing any concomitants which may cause interferences.
3. Before setting the AAS to zero, use a clean solution of distilled water. Change the water frequently, to avoid a buildup of iron in the rinse solution.

ANALYTICAL CAPABILITIES

Determination Limit (ppm) 5

Precision, at the 95% confidence limit (2σ), at 10X determination limit (50 ppm) is 8 ppm (absolute).

Silver Ag

STANDARD SOLUTIONS

Use 100 ppm solution prepared from 1000 ppm mixed custom stock solution to prepare working standards of 0.5, 1.0, 2.0 and 4.0 ppm.

INSTRUMENT PARAMETERS

Lamp Current (ma)	2.5
Wavelength (nm)	328.1
Spectral Band Pass (nm)	0.5
Background Correction	ON
Flame Description Air-acetylene, oxidizing, fuel lean, blue	

WORKING CONDITIONS

Sensitivity
1 ppm Ag solution reads 0.200 absorbance
Calibration
Set 1.00 ppm to read 1.00
Working range
0.5 to 4.0 ppm

NOTES

1. The higher salt content of the acid digested samples (dilution factor 25) may cause viscosity problems and/or burner clogging. Rinse well between samples.
2. Assay samples received as chemical leaches must not be diluted with HNO_3 which may cause a precipitate to form. Use water for dilutions and determine concentration by flame AAS as soon as possible. Normal first dilution is 5/500.

ANALYTICAL CAPABILITIES

Determination Limit (ppm) 2

Precision, at the 95% confidence limit (2σ), at 10X determination limit (20 ppm) is 1 ppm (absolute).

Cadmium Cd

STANDARD SOLUTIONS

Use 100 ppm solution prepared from 1000 ppm stock Cd solution to prepare 0.5, 1.0 and 2.0 ppm working standards.

INSTRUMENT PARAMETERS

Lamp Current (ma)	3.5
Wavelength (nm)	228.8
Spectral Band Pass (nm)	0.5
Background Correction	ON
Flame Description Air-acetylene, oxidizing, fuel lean, blue	

WORKING CONDITIONS

Sensitivity
1 ppm Cd solution reads 0.540 absorbance
Calibration
Set 1.00 ppm to read 1.00
Working range
0.5 to 2.0 ppm

INTERFERENCES

Background correction is required because of low resonance wavelength.

ANALYTICAL CAPABILITIES

Determination Limit (ppm) 2

Precision, at the 95% confidence level (2σ), at 10X determination limit (20 ppm) is 2 ppm (absolute).

OVERVIEW OF TRACE ELEMENT DETERMINATION BY ICP OPTICAL EMISSION SPECTROSCOPY

Introduction

Inductively coupled plasma-optical emission spectroscopy, ICP-OES, is employed for the determination of a number of trace elements in geological materials. The ICP-OES packages offered by the Geoscience Laboratories (GLOGS) include:

Aqueous Scan: The Geoscience Laboratories is able to accept aqueous samples for analysis on the JY48P ICP Spectrometer. No sample preparation is required and simultaneous determination of up to 36 elements is possible. The available elements are Sn, Mo, W, B, Zn, P, Pb, Co, Ba, Sc, Cr, Mg, V, Nb, Ca, Ag, Ti, Dy, Y, Eu, Sr, Gd, Ni, Ta, Mn, Fe, Si, Al, Be, Cu, Yb, Zr, Sm, La, Nd and Ce.

Trace 2 (T2): Rock pulps are prepared for analysis by acid digestion. The elements available in the Trace 2 package are: Be, Sc, Nb, Mo, V, Sr, Y, Co, Cu, Ni and Zn. Tungsten is also offered (at relatively high determination limits). Ce, La and Nd are offered as options; Zr, normally determined by XRF, is also available. The acid resistance of most Zr-containing minerals make ICP-OES analysis of solutions unsuitable for routine reporting of this element.

TSPA: The Tentative Spectroscopic Analysis package, run on rock pulp solutions prepared by acid digestion, provides semiquantitative analysis of 26 elements including Al, Ba, Be, Ca, Ce, Cr, Co, Cu, Fe, La, Pb, Mg, Mn, Mo, Ni, Nb, Nd, P, Sr, Ta, Ti, W, V, Y, Zn and Zr. Results are reported in terms of concentration **ranges.**

The operating concepts of inductively coupled plasma-optical emission spectroscopy are as follows:

(1) A high temperature excitation source is produced by the interaction between a radio-frequency field and a flow of argon gas. The interaction results in the ionization and excitation of the Ar to produce a plasma (or "flame"), which can attain temperatures in the range 8000-10000°C. At these temperatures, any sample which is introduced into the plasma will be vapourized, atomized, ionized and excited to emit radiation.

(2) The emitted light is dispersed by a grating in an optical system and the intensities of the spectral lines are measured, generally by photometric means, although photographic recording can be used. Instrumentation typically consists of either (a) a scanning monochromator with a single detector placed behind an exit slit on the Rowland circle (sequential measurement), or of (b) a polychromator with a number of photomultiplier detectors positioned behind fixed slits cut along the optical axis providing simultaneous wavelength-selective detection (direct reader).

(3) The ICP-OES spectrometer in the Geoscience Laboratories is a Jobin-Yvon JY48P direct reading instrument, employing a holographic grating, with 36 channels dedicated to elements of geological interest. These elements, along with their "channel numbers" and first order analytical wavelengths are listed in Table ICP.

(4) The JY48P instrument employs a PlasmaTherm source, generator and torch, with maximum plasma power of 2500 watts. Standard operating conditions average 1800 watts. The source system is not under computer control, and all settings must be established and reproduced manually. Although other nebulizer systems are available, the Geoscience Laboratories has consistently used a concentric glass nebulizer (Meinhard C3 type) with high salt capability. This nebulizer, along with a glass spray chamber and quartz torch are used for sample introduction, aerosol formation and excitation.

The torch unit is mounted in a "torch box" whose position relative to the entrance slit of the polychromator can be adjusted with a universal stage. As with the plasma source, torch position and optimal signal collection are under manual control.

TABLE ICP1. ANALYTICAL WAVELENGTHS AND CHANNELS ON JY48P ICP-OES SYSTEM

Fixed Channel Elements - Wavelengths (Å)

CH#	Element	Wavelength(Å)	Order
1	Tin	1899.26	1
2	Molybdenum	2020.30	1
3	Tungsten	2079.11	1
4	Boron	2089.59	1
5	Zinc	2138.56	1
6	Phosphorous	2149.14	1
7	Lead	2169.99	1
8	Gadolinium	3422.46	1
9	Cobalt	2286.16	1
10	Nickel	2316.04	1
11	Barium	2335.27	1
12	Tantalum	2400.63	1
13	Scandium	2552.37	1
14	Manganese	2576.10	1
15	Chromium	2677.16	1
16	Iron	2739.55	1
17	Magnesium	2798.06	1
19	Vanadium	2924.02	1
20	Aluminum	3082.15	1
21	Niobium	3094.18	1
22	Beryllium	3130.42	1
23	Calcium	3158.57	1
24	Copper	3247.54	1
25	Silver	3280.68	1
26	Ytterbium	3289.37	1
27	Titanium	3372.80	1
28	Zirconium	3438.23	1
29	Dysprosium	3531.70	1
30	Samarium	3592.60	1
31	Yttrium	3710.30	1
32	Lanthanum	3794.78	1
33	Europium	3819.67	1
34	Neodymium	4061.09	1
35	Strontium	4077.71	1
36	Cerium	4137.65	1

(5) The instrument is equipped with a Digital 11/23 computer with 128 Kbytes of memory, dual RXO2 floppy disk drives, DECWRITER III (LA120) and Tektronix 4006-1 (video) terminals. The software, provided by the Instruments S.A., (Metuchen, N.J.), provides full control of the detection parameters (e.g. integration time, time between successive integrations, number of replicate integrations). It also employs specialized routines for establishing analytical programs under specific conditions, regression analysis for calibration curve generation, plotting, background correction, matrix interference correction, entrance slit scans (profiles), blank subtraction, detection limit calculations and data acquisition, conversion and retrieval.

When not used to operate the spectrometer, the computer can be used as a general purpose device, running programs in FORTRAN, BASIC and MACRO languages. It can also be used for general file manipulation and text-editing. Off-line programs have been written for report generation and the preparation of TSPA worksheets and certificates. These programs use the ASCII data files created during spectrometer operation.

(6) The magnitude of the signal reaching a particular channel detector is dependent on the line intensity. This, in turn, is dependent on the concentration of analyte in the sample, as well as instrument conditions such as plasma power, rate of sample uptake, etc. The signal is also dependent on intensity contributions from other elements present in the sample - from direct and partial line overlap, continuum emission and background effects. Instrument software allows the operator to correct for many of these interferences through the use of background correction and interference correction coefficients.

The magnitude of the transduced photomultipler signal is controlled by the sensitivity of the detector. The JY48P permits separate control of the sensitivities for all channels by adjustment of switches on voltage control cards. Channel response is set in accordance with the expected abundance of the analyte in "normal" geological samples.

(7) The general operation of the system for the analysis of samples is described by the schematic diagram shown below. Features include:

- source and sample delivery under manual control;
- spectrometer under partial computer control, i.e., entrance slit position (profile scanning), channel profile selection (for external scanning), polychromator data acquisition (at all channels).
- manual control of detector sensitivities.
- detection under computer control, i.e., replicates, integration time, flush and delay times, etc.;
- machine language raw data files (*.RAW) for all channels and at all slit positions (for background

correction) stored automatically in polychromator data acquisition routines;
- ASCII analytical data files (*.DAT) are program controlled "translations" of the raw data files. The *.DAT files, obtained by processing the raw intensities through software TABLE files (*.TAB), contain information as intensities (counts) or concentrations for selected elements. These data can also be corrected for background or interferences.
- computer-controlled access of *.DAT files for implementation of regression routines, detection limit calculations;
- all programs, routines, *.RAW, *.DAT files are stored on floppy disks.

Computer Management - Software Control

Introduction to the Computer

The DEC 11/23 system is used for instrument control and for data processing and management using software available from the manufacturer. Because the application software is written in FORTRAN language, externally developed programs can be used to access the datafiles produced by the system and the computer used for the generation of analytical reports and certificates.

The system employs two floppy disk drives: the left-hand drive (LHD) is generally used for operating system files and the right hand drive (RHD) is used for analytical programs (*.TAB files), data and text files. The LHD is identified by name SY:, and the RHD by name DY1. Floppy disks are easily damaged, and the information stored on them cannot be retrieved if the disks are mishandled. Back-up copies should be made of all system disks every 6 months. When not in use, disks must be stored in the cases provided.

To use the computer, the system disk is placed in the LHD. To activate (i.e., BOOT) the computer, all three switches at the main computer are switched off and on again. Alternatively, with all switches on, the instruction 173000G is typed at the Decwriter.

It is not possible to boot the system from the video terminal, although once activated, control can be passed to this terminal by typing:

```
R CHTERM [R]
```

This instruction can be used to transfer control back and forth between terminals as long as the computer is in the RT-11 operating system.

NOTE: In the following pages, all instructions to the computer are underlined. It is assumed that all commands are followed by a carriage return [R].

Once the computer has been booted, the system requests the operator to input the date. Enter

```
XX-MON-YY
```

where XX = day, MON = three letter abbreviation of the month and YY = last two digits of the current year, e.g. 17-AUG-87.

The time can also be entered in the format

```
HR:MN:SC
```

where HR = hour, MN = minutes and SC = seconds, e.g. 14:30:20.

Formatting and Initializing a New Disk

Any new floppy disk to be used in the system must be formatted and initialized. To do this, the new disk is placed in the RHD and the system instructed:

```
R FORMAT
```

The system responds with a request for the location of the disk to be formatted by an asterick cursor (*), and operator answers:

```
DY1:
```

Since the operator may wish to re-format a disk which had been used previously, the computer asks for assurance that formatting is desired, i.e.,

```
ARE YOU SURE?
```

If sure, the answer Y is typed; if not sure, N or Ctrl-C (press the control [Ctrl] key and depress the C). To double-check that an "old" disk has no files you wish to retain, the operator can check the disk directory by command DIR DY1: to obtain the directory listing.

When the disk has been formatted, the system returns to the routine cursor (*) and waits for further instructions. To exit from the FORMAT routine, the operator types Ctrl-C; the system returns to the RT-11 operating system which responses with the '.' type cursor at the left margin.

The disk is now initialized using one of several instructions:

```
INI/BAD DY1:
INI/BAD/SEG:8 DY1:
INI/BAD/VOL DY1:
INI/BAD/VOL/SEG:8 DY1:
```

The first is used to initialize a **single density** disk with no volume identifier; the second, also with no volume identity, is used for a **double density** disk. Inclusion of the **VOL** part ot the command allows the operator to assign a **volume number and owner identity** to the disk. The **SEG:8** permits a greater number of files to be stored on the double density disk. Including **BAD** into the instruction allows the system to seek out "bad" blocks (defects) on the disk and identify their location.

After the initialization command the system asks:

```
ARE YOU SURE?
```

and, after a Y response, carries out the procedure. When initialization is complete, the system returns to the RT-11 operating system.

The Directory

After initialization, the operator can confirm the number of available storage "blocks" by typing

`DIR` or `DIR DY1:`

To obtain a directory of the system disk, the command is `DIR SY:`.

Alternate directory instructions include:

```
DIR/BAD DY1:
DIR/VOL DY1:
DIR/BRIEF
```

The first searches out the bad blocks, the second gives volume number, owner as well as file information. The DIR/BRIEF command yields an abbreviated directory - useful for disks containing many files.

Disk Management: Copying, Deleting and Viewing

COPYING FILES

Copying files from the disk at drive SY: to the a new initialized disk situated in drive DY1: is carried out as indicated below:

(1) Search the directory of the disk at SY:

```
DIR SY:
```

(2) Note files to be copied.

(3) Files may be copied one by one using the instruction:

```
COPY SY:XXXXXX.TYP DY1:
```

where XXXXXX represents the 6-character alphanumeric name of the file, and TYP represents its type, i.e., RAW = raw data, DAT = ASCII data, TAB = tables, etc. The operator must pay attention to the punctuation and spacing in the instruction, e.g. the period (.) between name and type (or extension).

The system then types out the name of the file and copies it in the direction indicated in the instruction. Reversing the SY: and DY1: addresses will reverse the direction of the copy.

(4) In order to copy many files of the same name, but different type, e.g., XXXXXX.**RAW** and XXXXXX.**DAT**, a wild card instruction can be used. An asterisk is used to represent the type or extension. For example,

```
COPY SY:XXXXXX.* DY1:
```

Similarly, to copy files of the same type, but different names, the wild card (*) can be used to represent the name. For example:

```
COPY SY:*.TYP DY1:
```

(5) All files, with the exception of systems files (type = **.SYS**) can be copied with the use of a double wild card, e.g.,

```
COPY SY:*.* DY1:
```

(6) The instructions given above assume that the name and type of the file will not be changed in the copy. Files can be renamed in the copy command by the following instruction.

```
COPY SY:XXXXXX.TYP DY1:YYYYYY.TYP
```

A copy of a file can be made on the **same** disk in this fashion, e.g.,

```
COPY DY1:XXXXXX.TYP
   DY1:YYYYYY.TYP
```

(7) The instruction given in (5) above, results in the indiscrimate copying of all files. In order to exercise some control over the files to be transferred,

a special command can be appended to the copy instruction, i.e.,

```
COPY SY:*.* DY1:/Q
```

The name of each file to be copied appears at the terminal and the copy instruction accepted or ignored on the basis of the Y or N response (a carriage return is equivalent to N).

(8) To copy systems files *.SYS, the instruction is:

```
COPY/SYS SY:*.SYS DY1:
```

or

```
COPY/SYS SY:*.SYS DY1:/Q
```

To copy all files, including the systems files, as in the case of duplicating a systems disk, the instruction will be:

```
COPY/SYS SY:*.* DY1:
```

or

```
COPY/SYS SY:*.* DY1:/Q
```

(9) In the case of duplicating a systems disk, it is important to copy over the **BOOT** routine. The following command sequence is used:

```
COPY/BOOT SY:DYMNSJ.SYS DY1:
```

```
COPY/BOOT DY1:DYMNSJ.SYS DY1:
```

Another utility on the operating system disk allows for copying of large numbers of files, for example when archiving data files.

(1) A new disk is formatted and intialized (if required).

(2) The command is given R PIP, and the system responds with the asterisk cursor (*).

(3) The system disk is removed from the LHD and replaced with the disk to be copied (or from which files are to be copied). The new disk stays in the RHD.

(4) The instruction is then given:

```
DY1:*.*=SY:*.* or DY1:*.*=SY:*.*/Q
```

In the case of the former, all (non-system) files will be copied; in the latter each file will be listed and depending on the Y or [R] (no) responses, copied or not. Once all the files have been copied, the operator places the systems disk back into the LHD and types

```
Ctrl-C
```

The system exits the PIP routine, returning to the system cursor (.).

DELETING FILES

In order to delete files from any disk, the disk name, as well as the name and type or appropriate wild card can be used, just as in the copy instructions. The /Q instruction can be used to avoid indiscriminate deletion. Some of the command types are listed below (the address is SY: but DY1: could also be used):

```
DEL SY:XXXXXX.TYP

DEL SY:XXXXXX.*    or   DEL SY:XXXXXX.*/Q

DEL SY:*.TYP            DEL SY:*.TYP/Q

DEL SY:*.*              DEL SY:*.*/Q
                        (safer with /Q)
```

In order to prevent all files from being erased, or to remind the operator what is being erased, the system types:

```
                                FILES DELETE
                                SY:XXXXXX.T
```

and awaits a Y or [R] to complete the instruction.

RECOVERING A DELETED FILE

A deleted file can be recovered if, and only if, no further data have been written to disk since the deletion occurred.

Type the following commands to recover a file deleted from a disk in the right hand drive:

```
R DIR
```

DY 1:/Q/B/O ... prints out the deleted file information

Note the starting block number (76 used as an example) for the particular file you are retrieving, thus:

```
B4.RPO 6 10-SEP-84 76
DY 1:/Q/B ... prints out deleted file information
```

Note the size (150 used as an example) of the file, thus:

```
DW:RAW 150 13-APR-84 104
CRTL C
R DUN
DY1: FILENAME.EXT = /C:START BLOCK
NUMBER: FILE SIZE
```

The data file should now have been recovered.

TYPING FILES

Files written in ASCII can be viewed in "English" or the appropriate alphanumerics while the system is in the RT-11 operating system. These include such filetypes as *.DAT, created by the JY48P software, and other files often created in the text editing mode, e.g., *.TXT, *.LST, *.BAK, etc. The file to be typed must be in the RHD to use the following series of instructions to work.

The instruction is:

```
TYPE XXXXXX.TYP
```

If there is a long series of related files to be be typed, wild-cards can be used to avoid unecessary repetition of instructions:

For example, for a long series of data files with common alphanumerics, e.g., AB0001.DAT, AB0002.DAT, AB0003.DAT, etc., the typed instruction would be:

```
TYPE AB*.DAT
```

If there is a series of files from AB0001.DAT to AB0800.DAT, and one wished to print out only from AB0500-AB0599, the instruction would read:

```
TYPE AB*5**.DAT
```

In some cases a code letter can be incorporated into a file name for convenience, i.e., B for blank, Q for quality control or S for standard. If all files of a specific code-type are required, then the instruction would read:

```
TYPE *S.DAT
```

and all .DAT files containing an "S" in the name will be typed.

CONTROL COMMANDS

In addition to the Ctrl-C command, which can be used to exit from any program and to return to the RT-11 monitor, there are a number of other Ctrl- commands which are useful.

Ctrl-O	- stops generation of output and returns system to monitor or program initialization;
Ctrl-U	- deletes a line of typing;
Ctrl-S	- temporary halt to output, awaits restart;
Ctrl-Q	- output restart;
Ctrl-A	- initialization of a subroutine, e.g., while in the spectrometer operation mode (program JY will return the operator to the first line of the program,

```
CURRENT POSITION?

JY48P:AN?CC?DL?DR?EN?FP?PL?PR?RG?TB?
```

Ctrl-X	- eliminates a string of instructions in the RT-11 text editor.

The Analytical Method - Theoretical Aspects

The analytical signal for any spectroscopic technique is generally made up of various contributions, i.e. the analyte signal, the background and matrix non-spectral interference and spectral interference. The latter contribution is very important in a number of spectroscopic techniques (i.e. optical emission, x-ray fluorescence and, to a lesser extent, mass spectrometry). The following discussion of interference corrections is centered around the problems observed in ICP-OES. The concepts, however, are applicable to all forms of spectral interference.

It is important to separate spectral interference from other forms of matrix interference. Spectral interference (line-overlap) results from the interaction of an interfering species with the analytical probe to produce a signal at the detector. This interaction is independent of the analyte identity and is only a result of analytical conditions. Non-spectral matrix interferences generally result from a physical or chemical interaction between the analyte and the interferent or a physical or chemical interaction between the interferent and the analytical conditions which effectively changes the conditions and results in a different level of interaction between analyte and the probe. Thus the matrix elements may alter the number of analyte species which are in detectable form, e.g. upsetting the analyte ion/atom equilibrium and resulting in signal enhancement or suppression. The matrix components may also cause physical flow problems, aerosol formation problems, etc.

If, for example, one examines the physical/chemical steps that occur in taking the analyte from the sample tube to the detection of radiation in an ICP experiment, it is possible to identify many sources of potential non-spectral interference.

(1) **Transport of sample to nebulizer:**

Whether one relies on the natural uptake rate of the solution or the use of a peristaltic pump, the viscosity of the sample will have a bearing on the rate of analyte delivery to the plasma. Reduction in flow will generally result in signal depression.

(2) **Nebulization of sample:**

The rate of aerosol formation in the nebulizer will depend on the total salt content in the sample solution. Reduction of sample flow for high salt samples or nebulizer blockage due to precipitation will probably result in signal depression.

(3) **Aerosol in the spray chamber:**

The design of the spray chamber, the temperature of the spray chamber and the nature of the sample will determine the droplet size distribution in the aerosol. This in turn will determine the amount of sample which can be swept into the plasma.

(4) **Processes in the Plasma:**

- Vaporization of solvent;
- Vaporization of sample salts;
- Atomization of sample components;
- Ionization of sample atoms;
- Recombination of atoms to form transient species;
- Excitation of atomic species;
- Excitation of ionic species;
- Excitation of molecular species;
- Oxide formation

The efficiency of these processes will depend on the flow rate of the sample through the instrument and the rate of delivery of sample vapor to the plasma, physical conditions of the plasma, e.g., temperature. Because of the very high temperature of the argon plasma compared to that achieved by a gas-oxidant flame in AAS, chemical recombination (oxide formation) is generally minimized and ionization and excitation efficiencies are expected to be high. However, the presence of relatively high concentrations of sample elements in the plasma can affect these efficiencies. The presence of large amounts of easily ionized species can upset the ion-atom equilibrium. The energy requirements for the processes may be high enough to lower plasma temperature and result in poorer efficiency of the processes. The additional excitations may contribute to the background.

A single element in a solution will produce a series of emission lines at different wavelengths. These result from the excitation of outershell (valence) electrons into unoccupied "upper" energy states (orbitals). The resulting atom/ion energy state is unstable, and the electrons lose the energy by returning to their original "ground" states. The energy lost (emitted) will be equal to the difference between the upper and ground state energies and will appear as specific wavelengths of radiation. These in turn can be dispersed by an optical device (prism or grating) and the level of emission measured at a photo-sensitive detector such as a photomultiplier tube or diode array. The number of emission lines can be very large, especially for elements with relatively high atomic number, as there is generally a large number of accessible upper energy states available for the excitation.

The wavelength of the emitted light is related to the energy difference between states. The relative intensities of the emitted lines (for a given, constant analyte concentration) is related to the energy state populations and transition probabilities). In the absence of spectral or non-spectral matrix effects, the intensity (I) of the emitted light for a defined analyte at a given wavelength will be directly proportional to the concentration of the analyte (C) in the sample.

$$I = k(C)$$

Furthermore in a system containing pure analyte, the signal (S) obtained from the detector will be linearly dependent on the intensity of the emitted light

$$S = k'(I) + B = k'k(C) + B = K(C) + B$$

where B = background contribution from sample matrix, e.g. solvent, and from the instrument (stray light, electrical noise, etc.).

Since we use calibration curves to convert analytical signals to concentration, it is more convenient to represent C as a function of S, thus:

$$C = A1\ (S) + A0$$

where A1 and A0 are the appropriate slope and intercept calibration coefficients respectively.

At high analyte concentrations, deviations from linearity can occur (due to detector effects, or due to nonspecific matrix effects caused by the analyte itself) and the calibration function is best described by a polynomial expression:

$$C = A2\ (S^2) + A1\ (S) + A0$$

or

$$C = A3\ (S^3) + A2\ (S^2) + A1(S) + A0$$

In a complex system containing a large variety of emitter atoms and ions, there will be a large number of spectral lines. These lines have a very narrow natural band width, but do experience a degree of broadening (Doppler effects, etc.). It is natural to expect that any given analyte line will have a relatively large number of lines due to concomitant elements nearby. It is also quite probable that a concomitant can have a line at exactly the same wavelength as that of the analyte (direct overlap), or close enough to it to be virtually inseparable by the optical system of the spectrometer.

It can be shown that for all but the cases of direct overlap, the ability to separate the lines will depend on the band-width of the lines, the degree of separation, and the slit width of the exit slit (in the mask at the Rowland circle of the spectrometer).

Quantifying Interferences

The contribution from the interferent will manifest itself as an "apparent" concentration of analyte higher than that expected (the true analyte concentration).

$$ST = SA + SI$$

where ST = total signal, SA = analyte signal, SI = interferent signal contribution.

$$\begin{aligned} C &= A1(ST) + A0 = A1(SA + SI) + A0 \\ &= A1(SA) + A0 + A1(SI) = CA + A1(SI) \end{aligned}$$

where C = observed concentration and CA = analyte concentration.

The intensity contribution and therefore the signal contribution (SI) due to an interfering element at the analyte wavelength of interest will be directly and linearly dependent on the concentration of the interfering element in the sample (CI).

$$SI = a(CI) + b$$

Substitution of this into the concentration expression above results in:

$$\begin{aligned} C &= CA + A1(a)(CI) + A1(b) \\ &= CA + x(CI) + y \end{aligned}$$

where x and y are defined as A1(a) and A1(b), the first and zero order interference constants respectively. In normal applications, only the first order constant is expected to have analytical significance.

In the case of multiple interferents, we can write:

$$C = CA + SUM\{\ (x_i)(CI_i)\ \}$$

where x_i and CI_i represent the individual constants and concentrations of the i interfering elements.

Correcting Interferences

In the analysis of one or more elements and their interferents, the number of corrections that may need to be made can potentially be very large. Moreover, the presence of sequential interferences (A interferes on B which, in turn, interferes on C, etc.) and mutual interferences (A interferes on B, and B interferes on A) will complicate the system. It is therefore important to be able to select those interference corrections which will be significant for the determination of any analyte. This is especially important in cases where interference correction is done through the instrument software and where the number of permissible corrections must be minimized (in order to be able to accommodate a maximum number of elements).

Interference coefficients are relatively simple to obtain by the following sequence of steps:

(1) Calibrate the spectrometer over the element (analyte and interferent) concentration range of interest, using individual element standard solutions. (Individual element standard solutions are preferred as mixed element standards can yield in unrecognized interferences in the original calibration.)

(2) Nebulize intermediate and high concentration level individual element standard solutions.

(3) Convert intensity data to concentrations. The interference coefficient may be calculated from the

slope of the curve of analyte concentration vs. interferent concentration. It is possible to use a single high level concentration solution and to estimate the first-order interference coefficient from the ratio

$$x_i = \frac{\text{Apparent analyte concentration}}{\text{Interferent concentration}}$$

The use of more than one solution will distinguish between true spectral interferences and background contributions. For example,

Interferent Conc.	Apparent Analyte Conc.
blank	0.0 ppm V
100 ppm Fe	0.1 ppm V
1000 ppm Fe	0.2 ppm V
blank	0.0 ppm Mo
100 ppm Fe	0.1 ppm Mo
1000 ppm Fe	1.0 ppm Mo

The use of 100 ppm solely for the determination of an interference coefficient would predict coefficients of 0.001 for interference of Fe on Mo and V. However, use of both 100 and 1000 ppm Fe indicates that the effect of Fe on V is more background, whereas the effect on Mo is a true interference because the signal at Mo is proportional to the Fe concentration.

In the absence of sequential or mutual interferences, software (or manual) correction is straight forward. The appropriate analyte and concentration data are obtained from the calibration curves and the interferent contribution calculated and subtracted from the observed analyte concentration to give the "actual" analyte value.

In the case of sequential interferences, the correction is more complex. For example, consider a case where analyte A interferes on B (coefficient x1) and B interferes on C (coefficient x2). Therefore:

$$\begin{aligned}
CA(obs) &= CA(true)\\
CB(obs) &= CB(true) + x1\ CA(true)\\
&= CB(true) + x1\ CA(obs)\\
CC(obs) &= CC(true) + x2\ CB(true)
\end{aligned}$$

and

$$\begin{aligned}
CC(obs) &= CC(true) + x2\{CB(obs) - x1\ CA(obs)\}\\
CC(true) &= CC(obs) - x2\ CB(obs) + x1\ x2\ CA(obs)
\end{aligned}$$

Depending on the value of CA, and the magnitudes of x1 and x2, the final term in the correction may be significant, and should be included. Some software packages (e.g. that of the JY48P) do correct in sequence and rely on the order of entry of the correction coefficients (elements). Others use the original observed concentrations only. Sequential interference corrections may need to be corrected off-line.

Mutual interferences are illustrated by the following set of equations (for the example of mutual interference by analytes A and B):

$$\begin{aligned}
CA(obs) &= CA(true) + x1\ CB(true)\\
CB(obs) &= CB(true) + x2\ CA(true)
\end{aligned}$$

This is a pair of linear equations:

$$\begin{aligned}
CA(obs) &= \quad CA(true) + \quad x1\ CB(true)\\
CB(obs) &= x2\ CA(true) + \quad CB(true)
\end{aligned}$$

with solutions

$$CA(true) = \frac{CA(obs) - x1\ CA(obs)}{(1 - x1\ x2)}$$

and

$$CB(true) = \frac{CB(obs) - x2\ CB(obs)}{(1 - x1\ x2)}$$

Where the term x1x2 is very small, it can be ignored.

The system can also be handled by matrix algebra since the linear equations can be rewritten as:

$$[CO] = [A]\ [CT]$$

where [CO] and [CT] are column matrices of observed and true concentrations respectively, and [A] is a square matrix of the type

$$\begin{vmatrix} 1 & x1 \\ x2 & 1 \end{vmatrix}$$

To evaluate this matrix equation, one uses the inverse of the square matrix, i.e.,

$$\begin{aligned}
[CO] &= [A] \times [CT]\\
[A\text{-}][CO] &= [A\text{-}][A] \times [CT]\\
&= [CT]
\end{aligned}$$

In this example the inverse matrix [A-] is:

$$1 - x1\,x2 \qquad \begin{vmatrix} 1 & -x1 \\ 1 & \\ -x2 & 1 \end{vmatrix}$$

and the solution is found from the product:

$$\frac{1}{1 - x1\,x2} \begin{vmatrix} 1 & -x1 \\ -x2 & 1 \end{vmatrix} \begin{vmatrix} CA(obs) \\ CB(obs) \end{vmatrix} = \begin{vmatrix} CA(true) \\ CB(true) \end{vmatrix}$$

$$CA(true) = \frac{CA(obs) - x1\,CB(obs)}{(1 - x1\,x2)} \text{...etc.}$$

The advantage of the matrix approach becomes apparent in highly complex systems, such as the following theoretical example:

Five elements, A, B, C, D, E

A interferes on B, C, E	coefficients x1 x2 x3
B interferes on D, E	x4, x5
C interferes on A, D	x6, x7
D interferes on C	x8
E interferes on A, B, C	x9, x10, x11

Thus

$$\begin{aligned} CA(obs) &= CA(true) + x6\ CC(true) + x9\ CE(true) \\ CB(obs) &= CB(true) + x1\ CA(true) + x10\ CE(true) \\ CC(obs) &= CC(true) + x2\ CA(true) + x8\ CD(true) \\ &\qquad + x11\ CE(true) \\ CD(obs) &= CD(true) + x4\ CB(true) + x7\ CC(true) \\ CE(obs) &= CE(true) + x3\ CA(true) + x5\ CB(true) \end{aligned}$$

which in matrix form is

$$\begin{vmatrix} CA(obs) \\ CB(obs) \\ CC(obs) \\ CD(obs) \\ CE(obs) \end{vmatrix} \begin{vmatrix} 1 & 0 & x6 & 0 & x9 \\ x1 & 1 & 0 & 0 & x10 \\ x2 & 0 & 1 & x8 & x11 \\ 0 & x4 & x7 & 1 & 0 \\ x3 & x5 & 0 & 0 & 1 \end{vmatrix} = \begin{vmatrix} CA(true) \\ CB(true) \\ CC(true) \\ CD(true) \\ CE(true) \end{vmatrix}$$

A programmable calculator or computer program can be used to solve the system. Uncorrected concentration data from the spectrometer are corrected off-line before reporting.

Although it is possible to correct for all of the possible interferences in a system, including the sequential and mutual corrections outlined above, it may not always be convenient or even significant to do so. If omission of a particular correction factor will not appreciably alter the final concentration and/or the error inherent in exclusion is smaller than that obtained from instrumental precision, the correction can be ignored. This is typically the case when either the magnitude of the coefficient is very small, or the concentration of interferent is very low. Corrections due to sequential or mutual interferences are generally found to be very low and are almost always ignored.

To Correct or Not to Correct

The relative standard deviation contributed to a result by the omission of a particular interference correction can be written as:

$$RSD = \frac{x_i\,C_i}{CA(true)}$$

i.e., the ratio of the interference contribution to the "actual" or "true" analyte concentration.

It is possible to predefine a value of RSD, related to expected experimental precision, below which the interference is considered to be insignificant. Thus, for example, if we define significance at RSD = 0.01 (1%) then for a coefficient of $x_i = 0.01$ we can write:

$$00.1 = \frac{0.01\ C_i}{CA(true)}$$

The limiting ratio of interferent to analyte concentration is therefore 1. Conversely if the analyte concentration is expected to be more than the concentration of the interferent, the interferent can be ignored.

For example: Vanadium shows an ICP interference on aluminum with coefficient 0.15. Under normal circumstances this is a relatively high value for an interference coefficient and would not be ignored.

From the RSD criterion, we can estimate limiting concentration ratios for a series of RSD values.

RSD =		C(V)/C(AL) ~
1	(100%)	6.7
0.5		3.3
0.25		1.7
0.1		0.7
0.05		0.3
0.025		0.2
0.01		0.1

For levels of aluminum in silicate rocks of 5-15%, and acceptable precision levels of 5% (RSD = 0.05), the concentration of vanadium would need to be between 1.5 and 4.5% for the vanadium interference to have any significant contribution. As this concentration is not likely to occur in most silicate rocks, the vanadium correction can be ignored in the determination of Al in silicates.

Interferences and the Determination Limit

The significance of a potential interference can also be evaluated in terms of: (1) the determination limit or (2) practical detection limit for an analyte. Detection limits (instrumental) are generally based on the noise observed when a large number of replicate integrations are obtained during a single nebulization and represent instrument stability over a relatively short period of time. On the other hand, the determination limit, a much more realistic estimate of the sensitivity of the method, is based on 3 times the standard deviation obtained for replicate determinations of a low-level sample and may be degraded further by allowance for matrix effects.

As emission intensities are found to reproduce within 5-10% RSD from one nebulization to the next or from one day to the next a "practical detection limit" (PDL) can be defined as 10%(RSD) blank/background intensity, i.e., approximately 2 times the error equivalent to a 5% RSD in intensity. The determination limit (generally used in quoting analytical capabilities) and the PDL are often found to be approximately equivalent.

Since the acceptability criteria for a particular result can be expressed in terms of the determination limit (or PDL), we must account for matrix corrections which will affect or contribute to the determination limit.

We can write:

$$CA(sol) = A1\ SA + A0 + CM(sol)$$

CA(sol) = solution apparent analyte concentration; A1, A0 = calibration coefficients; SA = signal contribution from analyte; CM(sol) = concentration contribution to analyte from matrix = SUM(x_i C_i)). Rock-equivalent concentrations are obtained by

$$CA(rock) = CA(sol)\ X\ DF$$

where DF = dilution factor (normally DF=100 for 0.5 g sample in final volume of 50 ml).

If we accept a realistic error of 5% RSD in the analyte and interferent intensities, then the upper concentration limit in the apparent solution concentration, [CA(sol)+], will be equal to

$$[CA(sol)+] = A1(1 + 0.05)SA + A0 + (1 + 0.05)CM$$

and the error, [E+], will be

$$\begin{aligned}[E+] &= [CA(sol)+] - [CA(sol)] \\ &= A1(0.05SA)+0.005\ CM\end{aligned}$$

Similarly the lower concentration limit, [CA(sol)-] can be evaluated and the error [E-] defined as

$$\begin{aligned}[E-] &= [CA(sol)-] - [CA(sol)] \\ &= -A1(0.05SA) - 0.05CM\end{aligned}$$

The practical detection limit of the analyte, PDL, can be defined as twice the error in CA(sol), or more simply:

$$\begin{aligned}PDL &= [E+] - [E-] \\ &= [E+] + |[E-]| \\ &= 0.1(A1)(SA) + 0.1(CM)\end{aligned}$$

In the absence of any interference (CM=0), the analyte contribution to the practical detection limit of the analyte, PDL(A) can be defined as

$$PDL(A) = 0.1(A1)(SA)$$

In the absence of analyte, the matrix contribution to the practical determination limit of the analyte, PDL(M), can be defined as

$$PDL(M) = 0.1(CM)$$

Error in the determination of the matrix interferents and in the subsequent contribution of this error to the error in the observed analyte concentration will affect the overall PDL or determination limit of the method.

Example:

Consider niobium in a matrix containing 5% Fe, 4% Al, 4% Ca, 2% Mg and 0.2% Ti.

Calibration curve coefficient (A1) for Nb = 5.6^{-6}

Calibration curve coefficient (A0) for Nb = -0.5

Measured interference coefficients, x_i, for matrix elements on Nb:

x(Fe) = 0.000027
x(Al) = 0.00022
x(Ca) = 0.000030
x(Mg) = 0.00012
x(Ti) = 0.00018

Niobium blank intensity = 90000 counts

PDL(A) = 0.1 (90000)(5.6^{-6})
= 0.05 ppm
= 5 ppm-rock

From the interferent element concentrations expected in solution, C_i, i.e., C(Fe) = 500 ppm, C(Al) = 400 ppm, C(Ca) = 400 ppm, C(Mg) = 200 ppm, C(Ti) = 20 ppm, we can calculate the total matrix contribution, CM (where CM = SUM(x_iC_i).

Contributions:

x(Fe)C(Fe) = 0.0135 ppm solution
x(Al)C(Al) = 0.0880 ppm
x(Ca)C(Ca) = 0.0120 ppm
x(Mg)C(Mg) = 0.0240 ppm
x(Ti)C(Ti) = 0.0036 ppm

CM = 0.1411 ppm solution
= 14 ppm-rock

and

PDL(M) = 0.1(CM)
= 0.0141 ppm
= 1.4 ppm-rock

PDL = 0.05 + 0.0141
~ 0.06-0.07 ppm
= 6-7 ppm-rock.

Thus, the contribution of error in the determination of matrix components results in an effective PDL of ~6-7 ppm-rock in the matrix of interest.

We can use the expression derived previously to determine the relative importance of the matrix corrections, i.e.,

RSD = x_iC_i/CA

and if we accept a value of RSD = 1% as the limiting error contribution we can establish critical ratios of C_i/CA for the various interferents.

Interferent	**Critical C_i/CA**
Fe	370
Al	45
Ca	330
Mg	85
Ti	55

Consider an ICP-OES result at the Nb channel = 280000 counts

Apparent Nb solution concentration = 1.07 ppm.

Since we do not know the true analyte concentration, we assume that it is approximately equal to the apparent concentration. We can therefore estimate observed C_i/CA values and compare them to the the limiting interferent concentrations:

Interferent	**C_i/CA Limiting**	**C_i/CA Observed**	**Correction**
Fe	370	470	yes
Al	45	370	yes
Ca	330	370	yes
Mg	85	190	yes
Ti	55	20	ignore

We can examine the effect of ignoring interferences in greater detail. For example, if we correct the result for all five interferences:

[Nb]apparent = 1.07 ppm solution
[Nb]corrected. = 1.07 - 0.14
= 0.93 ppm solution.

The error in ignoring the total matrix contribution would be 15% RSD which is greater than would be allowed by conventional acceptability criteria.

Ignoring the contribution from Ti alone would result in a concentration of 0.93(±0.36) ppm with an error of 0.4%, i.e., less than 1% RSD as predicted by the critical ratio method.

Similarly, ignoring the contribution from Mg, Ca, Al and Fe would result in errors of 2.5%, 1.3%, 9.5% and 1.5% RSD respectively.

In some cases, the observed analyte concentration may not be a suitable approximation of the true analyte concentration and the limiting ratio method will not be suitable to judge the need for a correction. Another approach can be considered. It is possible to assign an arbitrary "cut-off" point below which interferences can be ignored. As a first approximation,

if x_i C_i 0.5 PDL(A)

the contribution can be ignored with minor contribution to total analytical error.

In the Nb example, 0.5(PDL(A)) = 0.025 and all but the Al could be ignored. Mg is a borderline case and the correction is included. The subsequent, partially corrected, Nb value would be 0.956 ppm (total error ~ 3.1% RSD). To reduce the error the "cut-off" value could be set at an even lower fraction of the analyte PDL(A) if desired.

From this limiting criterion, it is possible to estimate critical interferent concentrations for any analyte based on the PDL(A) and interference coefficient:

$$x_iC_i \le \frac{PDL\text{–}A}{2}$$

$$C_i(crit) = \frac{PDL\text{–}A}{2x_i}$$

Thus, for the Nb example, PDL(A) = 0.05 ppm solution (5 ppm-rock) the critical concentrations for a series of potential interferences are listed below:

Element	x_i	C_i(crit)-sol	C_i(crit)-rock
Fe	0.000027	925 ppm	9.25 %
Mg	0.00012	210	2.1
Ca	0.000030	830	8.3
Al	0.00022	114	1.1
Ti	0.00018	140	1.4
Ni	0.00018	140	1.4
V	0.10	0.25	25 ppm
Cu	0.00021	120	1.2 %
Nd	0.0012	21	2100 ppm (0.2%)

Summary

In the determination of elements by ICP-OES, the potential interferences can be summarized into four principal categories:

Major Interferent - Major Analyte
Major Interferent - Trace Analyte
Trace Interferent - Major Analyte
Trace Interferent - Trace Analyte

Given the relative concentration levels of most major and trace elements in geological samples, we are generally only interested in the interference of trace elements by major elements. To a limited extent we are also concerned with Trace-Trace interferences where the coefficient is very high.

It is important, however, to evaluate all the interferences critically for any given matrix type. The samples arriving at the Laboratories are varied and complex. What may be acceptable for a relatively barren silicate rock may not be acceptable for an ore or a mineral. Each case must be examined and where necessary, additional interference corrections used. The use of concentration ratios or PDL criteria become very important. A complete list of interference coefficients is on file.

THE TRACE 2 (T2) PACKAGE INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY

Introduction:

Given the extensive analytical potential and flexibility of ICP-OES, a wide variety of elements can be determined using this instrument. At the Geoscience Laboratories we have grouped many geologically important elements into the Trace 2 package. Usually these elements are at the ppm to ppb levels, but in some samples, from specific geological environments, they can be much higher.

Geologists use trace elements to monitor the genesis of rocks and evaluate process that affect rocks after formation. Elements such as Ni, Sc, Y, Nb, REE (Ce, La, Nd), Sr and V usually occur at trace levels in rocks and are used as discriminators to determine origin, tectonic setting or degree of alteration. Other elements such as W, Co, Be, Cu and Zn are used more specifically to assess rocks for ore potential.

An inductively coupled plasma source emission spectrometer (JY48+) is used to perform elemental analysis on samples which have been decomposed using a wet chemical (acid digestion) procedure.

The TRACE 2 (T2) package elements, their determination limits, optimum range, and precision are listed in Table OES1.

TABLE OES1.

Element	Determination Limit (ppm)	Optimum Range	Precision* (ppm)
Be	1	1 - 100	1
Co	5	5 - 1000	10
Cu	5	5 - 1000	10
Mo	10	10 - 4000	30
Ni	5	5 - 1000	10
Sc	2	2 - 100	5
V	5	5 - 500	10
Y	5	5 - 1000	20
Zn	5	5 - 1000	10
Options			
Ce	35	35 - 3000	70
La	5	5 - 2000	10
Nb	5	5 - 500	10
Nd	25	25 - 2500	50
Sr	5	5 - 10000	15
W	50	50 - 500	100

* Precision is quoted as the 95% Confidence Limit (ppm) for a value at 10X the determination limit.

Safety Advisory:

UNTRAINED OPERATORS SHOULD NOT ATTEMPT TO START OR USE THE EQUIPMENT WITHOUT PRIOR TRAINING.

There are five types of hazard associated with this apparatus: electrical, radiation, high temperature, noxious gases and physical hazard.

1. Electrical hazards can be encountered in three areas: the plasma power generator, the plasma torch compartment the spectrometer tank compartment and associated with various peripheral equipment like pumps, autosamplers and other special apparatus which may be set up to facilitate the analysis. The power generator is of particular concern because high voltages are retained on capacitors even when the power has been completely disconnected from the instrument. **DO NOT ATTEMPT TO GAIN ENTRY TO THE POWER GENERATOR WITHOUT PROPER TRAINING.** Other areas are protected by interlocks. **DO NOT OVERRIDE INTERLOCKS.**

2. Two types of electromagnetic radiation are of concern: radio frequency and ultraviolet. Radio frequency radiation has no known teratogenic effect, but can cause somatic damage and could affect eyesight by the absorption of radiation by the fluids of the eye causing a damaging increase in pressure within the eye. It is important to ensure that the plasma torch compartment is well shielded by inspecting the viewing and access ports. Operate the instrument with the door closed to make sure that the RF radiation cannot escape. The power transfer cable should be inspected to ensure that it is a tight fit and that no corrosion has occurred at the connecting points on both the in-

strument and on the plasma power generator (**EXPERIENCED TECHNOLOGISTS ONLY!**). Ultraviolet radiation is emitted by the plasma. **THE PLASMA SHOULD NEVER BE VIEWED DIRECTLY.** Even light from the plasma which is reflected from the source housing has a high level of ultraviolet radiation and direct viewing of this light should be avoided.

3. The plasma operates at extremely high temperatures. The interlocks protecting the plasma should never be overridden. The torch itself can become quite hot and sufficient time should be allowed, after extinguishing the plasma before disassembling the torch for routine inspection and cleaning. The plasma power tube runs at about 300°C and should be cooled at least 20 minutes prior to shutting the generator down at the end of the day or for inspection.

4. The exhaust gases from both the plasma compartment and the generator can be a source of both heat and noxious fumes. Both beryllium and ozone are emitted from the generator. The exhaust from the plasma can contain toxic materials from the samples. **THE EXHAUST FROM BOTH THE GENERATOR AND THE PLASMA MUST BE VENTED FROM THE ROOM AT ALL TIMES.** Remember to check the damper positions to ensure that sufficient exhaust velocity is being maintained.

5. Physical hazards can be encountered when moving or working around bottled gases. Exercise appropriate caution: secure the cylinders, use the valve caps, use properly designed carts to move the cylinders and use appropriate footwear.

Method:

The method consists of the following techniques:

1. Dissolution of sample using acid digestion technique.

2. Measurement of analyte concentration using the Jobin-Yvon JY48P ICP-OES instrument.

3. Calculation of results.

Apparatus:

- Jobin-Yvon JY48P simultaneous ICP source emission spectrometer
- Meinhard TR-30-C3 nebulizer
- Gilson Minipuls-3 peristaltic pump
- Gilson autosampler

Reagents:

- Argon gas
- Nitric acid, HNO_3, 10%

Procedures:

1. JY48P Start-up

1.1. Turn on the RF generator. A few seconds later, a "click" will be heard and that signifies the cooling water is being turned ON.

1.2. Switch the reflected power switch to 'OFF'.

1.3. Turn on the argon gas supply.

1.4. Connect the nebulizer tubing to the peristaltic pump and secure peristaltic pump tubing clamps.

1.5. Switch on Plasma, Nebulizer and Auxiliary gas flows by depressing buttons marked accordingly on the ICP front panel.

1.6. Nebulizer water and allow the system to purge argon for two or three minutes.

1.7. Set

- Plasma gas at 14 1pm
- Nebulizer gas at 0.75 1pm
- Auxiliary gas at 0.52 1pm
- Uptake rate of nebulization at 1 ml/min (pump setting @ 19)

1.8. Switch the nebulizer gas flow off.

1.9. Set tuning control in the front panel to MANUAL and obtain a reading of approximately 164 by adjusting with the white buttons at the top left corner.

1.10. RESET THE TUNING CONTROL TO AUTO.

1.11. Press the RF power button of the torch box ON.

1.12. Dial the forward power up to about 1 kW and ignite plasma by briefly pressing the ICP IGNITE button. STOP as soon as the plasma has ignited. After ignition is achieved, immediately switch the NEBULIZER gas flow on and increase the incident power to 1.8 kW. Switch the reflected power switch at the RF generator to the right (on).

1.13. If unsuccessful in igniting the plasma, purge the system with argon for two to three minutes and repeat the procedures starting at step 1.8.

1.14. If necessary, adjust reflected power to a minimum with the fine knob located on the right end-plate of the box.

1.15. BE PREPARED TO IMMEDIATELY PRESS RF OFF IN THE EVENT THE PLASMA EXTINGUISHES!

1.16. Let the system warm up for at least 45 minutes or until the inside chamber temperature remains fairly constant (monitored by a thermometer at the upper part of the front panel of the plasma box).

NOTE: Refer to diagram 13 in JY48P spectroanalyzer user's manual

2. JY48P Shutdown procedure

2.1. Dial the forward POWER slowly down to approximately 6 on the dial.

2.2. Press the RF OFF button on the front panel.

2.3. Depress the plasma and auxilliary gas flows (off).

2.4. Dial the forward POWER down to 0.

2.5. Flush the system by nebulizing deionized water for a few minutes.

2.6. Switch off the Nebulizer gas flow.

2.7. Let the RF generator to cool off for at least 15 minutes before switching the main supply off.

2.8. Turn off the peristaltic pump.

2.9. Disengage the clamps of the peristaltic pump and release the tubing.

2.10. Close the valve of the Argon gas supply.

3. JY48P Digital PDP-11/23 Computer Start-up

3.1. Insert JY48P system disk into left system drive (SY: or DYO:) and a data disk into the right drive (DY1:)

3.2. Boot up the system at the keyboard terminal by typing 173000G and press return. Additional information on the computer system is given in the Overview Section - page EA18-1 to EA18-13.

3.3. Enter Date (e.g. 12-Sep-89) and press RETURN.

3.4. Verify the date entered by Y (yes) or N (no).

3.5. Enter the Time (08:32:56) and press RETURN.

3.6. Verify the time entered by Y (yes) or N (no).

3.7. A "Dot" prompt will appear and that signifies the system is ready.

4. Routine Analysis

NOTE: Ensure that all plasma conditions, resistance settings for all analytes of interest and the parameter settings in the Table are correct.

4.1. At the "dot" (.) prompt, enter R JY48P and press return.

4.2. Enter current position (read from slit position dial on the upper part of the JY48P).

4.3. Enter Peak position. The "JY Main Menu" will now appear.

4.4. Enter "AN" for analysis.

4.5. Enter Table file name in the format of XXXXXX where X represents alphanumerical characters. (A *.TAB file is created previously and has to be on the data disk for execution. See Section 7 for Parameter-Table set-up).

4.6. Enter CHG to ensure the analytical parameters are right. Changes can be entered at this time.

4.7. Manual Analysis: enter ANA for sample analysis.

Example of typical routine run protocols (maximum number of samples for a batch of samples is 50):

a. Warm-up solutions: Do not enter sample ID's for these samples to avoid saving data on disk. This can be achieved by simply hitting the RETURN key.

b. Recalibration standards (if restandardization is necessary and requested as the mode). These ID should begin with CAL###, where ### must correspond to a LOW or HIGH standard as defined in the Table routine.

c. Rinse (10% HNO_3). (Normally sample ID is not entered so as not to store data on disk).

d. Blank solution (10%HNO_3). The sample ID has to begin with the letters BLK if blank subtraction is requested as the mode. (All samples following this BLK will be automatically blank corrected).

e. Check solution (normally its ID is CK###).

f. 10-15 routine samples.

g. Check solution.

h. 10-15 routine samples (if spaces are available).

i. Check solution (if spaces are available).

j. .... (check, samples, check, samples, check and so on).

k. 1 or 2 reference standards and/or calibration standards.

4.7.1. Enter CNCODFBSSD (see JY48P software manual for explanations).

4.7.2. Enter XX where XX = # of samples (maximum # of samples is 50).

4.7.3. Enter the sample identifiers according to the protocol required by the data reduction software programmes. (Refer to the JY48P software manual).

4.7.4. When all sample ID's have been entered and at the "ready?" prompt, put the nebulizer tubing into the first sample tube. Wait until the sample has been taken into the plasma and allow 20-30 seconds for equilibrium/stabilization, hit the RETURN key to begin the sample analysis.

4.7.5. When the sample analysis is finished, transfer the tubing (probe) to the rinse bottle. If the measurement is OK, enter Y. Otherwise enter N for a not OK answer and the prompt will prompt for "REMEASUREMENT". Simply hit RETURN and analysis will continue.

4.7.6. At each "ready?" prompt repeat the process until all of the samples have been analysed and the prompt "ANA?CHG?END?" appears.

4.7.7. Enter END to end the analysis and return to beginning of JY48P routine.

4.8. Use of the Autosampler

Enter ANA for sample analysis and include AS in analytical command string.

a. Connect rinse solution tubing to peristaltic pump and secure clamps.

b. Enter command string (include AS) and press return.

c. Enter 1 at the prompt "# samples?".

d. Hit return at the prompt "1 sample name?".

e. Enter E to exit at the prompt "Ready?". This will 'move' the light from ACQ to RESET on the upper front panel of the JY48P.

f. Check the adjustment of the pipette tube of the autosampler by slowly lowering it into the snap tube with the Auto-Adj switch. Check both the depth to which the probe reaches in the Snap tube and the centering of the probe as it enters the Snap tube.

g. At the base of the autosampler unit, set:

- power switch to ON
- function switch to EXT
- autosampler pipetting unit
- Auto-Adj switch to AUTO (up) position
- Op-Load switch to OP (up) position

h. Enter ANA at "ANA?CHG?END?".

i. Enter CNCODFASBS (see JY48P software manual for explanations).

j. Enter XX where XX = # of samples. MAXIMUM # of samples is 50.

k. At the prompt "X sample name?" where X = sequence of sample number, start entering the sample identifiers. (Refer to the JY48P software manual).

l. At the last sample ID entry, ensure all of the above have been done before hitting RETURN. At this point, the pipet of the autosampler will go into the first sample tube and the analysis will begin.

5. System Calibration

5.1. Set/check all plasma conditions and resistance settings for the analytes of interest.

5.2. Run the calibration standards:

- blank (deionied water)
- blank (10% HNO_3)
- calibration standards (see additional notes)

5.3. In the JY48P mode, enter RG for regression routine.

5.4. The computer first asks for a table filename (there is no need to answer this question; just hit RETURN) and then requests a standards filename. See JY48P software manual for details.

5.5. Enter INT at the RG mode.

- enter the standard numbers (1 to 20) and the corresponding data filenames.
- when all standard files have been entered and "standard #?" prompt is displayed hit RETURN to end intensity entry and the computer will return to the RG mode.

5.6. Enter CON:

- channel by channel, enter the standards numbers (defined at 5.5) and the corresponding concentrations (units of concentrations used here determine units output in analysis).

5.7. Enter CAL at RG mode and 1 at the prompt "DEGREE?" for first order curve.

5.8. Enter N (RETURN) for normal weighing (equal weighing of all points minimizes absolute error).

5.9. Enter Y (yes) to save curve in memory or N (no) not to save curve.

5.10. Enter VER or MOD for verify or modify the calibration results (see JY48P software manual for further explanation). At the end of VER or MOD mode, make sure to CAL (calibrate) and accept (Y for yes) the calibration curves.

5.11. Repeat steps 7-8 until calibration is complete.

5.12. When all calibration curves have been accepted, enter EN to exit the RG routine.

5.13. Enter Y (yes) to save the standard file. If this is not done, all files will be lost and you must repeat the entire calibration process.

5.14. Enter XXXXXX to store the standards file on disk for later use (XXXXXX = alphanumerical characters for the standards filename).

5.15. Enter Y (yes) to save the recent changes (updated curves) in the Table on disk.

5.16. Enter XXXXXX (the name) to store Table parameters on disk for later use. If no name is given, parameters are not saved on disk, but are still retained in memory.

NOTE: In the Table file, a low and a high standard are defined for each analyte of interest under CAL### naming convention (e.g. CAL002, CAL004). The standards on the following page are used.

When system restandardization is required, the option CA has to be included in the AN (analysis) mode.

With the same plasma source conditions, the gains and offsets associated with the restandardization calculations should change by less than 10% (generally within 5%). However, if the change is greater than 10%, the following operating parameters should be considered and checked: nebulizer clogging, changing plasma gas flows, contamination of standards, incorrect measurement conditions (integration time etc.), peristaltic pump problems, incorrect PMT resistance settings, exhaust fan problems, incorrect slit position, misidentified calibration standards, uncleaned torch, etc.

Element	Lowstd # Conc.	Highstd Conc.
Tungsten	1,0	8,10
Beryllium	2,0	3,0.1
Cobalt	2,0	4,10
Nickel	2,0	4,10
Copper	2,0	4,10
Vanadium	2,0	4,10
Strontium	2,0	4,10
Scandium	2,0	4,1
Yttrium	2,0	4,1
Molybdenum	2,0	4,1
Zinc	2,0	5,10
Barium	2,0	5,10
Chromium	2,0	5,10
Niobium	2,0	5,1
Zirconium	2,0	5,1
Cerium	2,0	5,1
Magnesium	2,0	6,500
Phosphorus	2,0	6,50
Iron	2,0	
Calcium	2,0	7,1000
Aluminum	2,0	7,1000
Titanium	2,0	7,80
Manganese	2,0	7,80
Tantalum	2,0	10,10
Lead	2,0	9,10
Lanthanum	2,0	9,10
Neodymium	2,0	9,10

To monitor the drift of the instrument, check solutions are usually run every 10-15 samples within a batch analysis. When a particular analyte drift is greater than 3 times the standard deviation of its statistical data, restandardization of the system is necessary or the above mentioned operating parameters should be checked.

7. Parameter-Table Set-up

7.1. Enter TB at the "JY main menu".

7.2. When setting new parameters, simply hit RETURN at the next prompt. Otherwise, enter the Table filename of the routine (stored on system or data disk as *****.TAB).

7.3. For daily routine T2 and TSPA packages, see the additional notes for the parameters that are currently used in this laboratory. Details of setting up these parameters are listed in the JY48P software manual (ref. 12.0).

8. Report Generation

8.1. For the T2 package, refer to details listed in "GENERATION OF T-2 FINAL REPORT", page EA18-21.

8.2. For TSPA package, refer to details listed in "GENERATION OF THE TSPA CERTIFICATES AND/OR WORKSHEETS", page EA18-25.

NOTE: If semi-quantitative analysis is required to be reported in ppm instead of in percentage use the program JANET in place of WORCER.

To report results from the calcium and magnesium package (water samples), run the analysis under CAMG.TAB to generate the Ca and Mg concentrations on the data disk. Then use the program "WATER.SAV" to generate the report.

9. Digital PDP-11/23 Computer Shutdown

9.1. Exit the JY48P mode by entering EN at the prompt JY48P routine. A 'Dot' prompt will appear.

9.2. Remove both the JY48P system and the 'Data collection' disks from the two drives. Leave the doors open and the switches at ON positions.

9.3. Press the button "BREAK" on the keyboard terminal.

Quality Control:

The overall quality of analytical data for the Trace 2 method is as quoted in Table OES1. This has been devised from the Laboratories blind duplicate program over a 5 year period.

Quality control for the techniques which comprise the method are described below.

Preparation of check solution: After each batch of samples has been analysed, the remaining T2 rock solutions are collected.

When a sufficient volume (approximately 3 to 4 liters) has been collected, the solution is filtered and becomes a check solution for the instrument quality control. The following is the list of the concentration means and the associated standard deviations of that present solution.

Concentration	Mean (ppm)	Standard Deviation
Be	0.89	0.052
Co	36	0.51
Cu	99	1.33
Mo	-	-
Ni	105	1.15
Sc	24	0.47
Sr	303	3.06
V	199	1.95
Y	22	0.34
Zn	102	1.64

The above results are calculated on 60 observations, with the exception of Be which is based on 26 observations.

Aliquots of the check solution are analysed with each batch of samples using the routine run protocol and the results are compared against those in the above table. The number of standard deviations of the check solution away from the mean is calculated using the formula:

(observed check - solution conc. - mean)/ s.d.

If the analytical error is normally distributed, 95% of the results should be between 2 times s.d. When one or more analytes in the check solutions fall outside 3 times s.d., the operating parameters outlined in section 5 should be checked and restandarization of the system is necessary.

If reagent blanks are less than the method determination limits, no further action is necessary. However, if one or more elements in the reagent blanks are greater than the instrument detection limits, data will then be submitted to the Supervisor or ICP Spectroscopist for further decision.

Numerous in-house (MRB) and international SRMs of varying geological compositions including GA, BHVO1, MRG-1, SY2, SY3, NIMG, NIMD, NIMP, NIML, NIMM, NIMS, GSS1-8 etc., are used to monitor accuracy and precision within the ICP-OES laboratory.

Productivity:

A technician should be able to complete 150 samples per day.

Additional Notes:

1. The computer manufacturer recommends that the system boot be through the keyboard terminal rather than through the system switches. Generally, the system is left with the two drive doors open and all the switches at the ON (UP) positions.

2. To minimize the interelement spectral interferences, a series of calibration standards is prepared from a serial dilution of stock standards. There are six stock calibration standards prepared for the daily routine analysis.

a.	100W	100 ppm W
b.	A	100 ppm Co, Ni, V, Cu, Sr 10 ppm Sc, Y, Mo
c.	B	100 ppm Zn, Ba, Cr 10 ppm Nb, Be, Zr, Ce
d.	MN	(minor)500 ppm Mg 50 ppm P
e.	MJ	(major)1000 ppm Fe, AL, Ca 80 ppm Mn, Ti
f.	C	100 ppm Pb, La, Nd
g.	Ta	100 ppm Ta

3. To maintain optimal analytical precision, the following procedures are recommended:

a. clean the torch.

b. clean and unclog nebulizer.

c. analyte profiles (top and bottom) should be checked periodically.

d. ensure the "wick" (for guiding the drain) in the spray chamber is in the correct position. Small fluctuations in the pressure within the spray chamber substantially alter the emitted signal. (The drain bucket should be emptied periodically - never allow it to get more than half full).

e. gas lines to the torch and nebulizer should be clamped with snapper hose clamps (critical for good RSD).

f. periodically monitor the gas flow rate to ensure constant flow.

g. change the sample delivery tubings periodically and check the uptake rate (1 ml/min distilled water).

h. there should be no cracks in any of the rotometers, gas lines (located inside the torch box, left hand side).

APPENDIX A
GENERATION OF T-2 FINAL REPORTS

Introduction:

The T2FORM programs produce the final T-2 job report forms. To do this, three programs must be run in succession; the programs T2CON, JOBFIL and T2FORM. The following describes how to use these programs.

The program T2CON creates a concentration file containing T-2 concentration data on the system disk. A maximum of 150 samples can be processed at one time.

The user runs the program JOBFIL to create two files: a file containing the sample identifiers and a file containing the geologists' names and job numbers. A maximum of 150 samples and 10 jobs can be processed at one time.

The program T2FORM prints out a signature-ready T2 form. All data are rounded to the nearest 1 ppm (rock). Any results less than the method determination limit are reported as the "minus" of the determination limit. Any results greater than or equal to one percent are reported to the nearest decimal with a 'P' appended to them.

(1) Insert the system disk for T2 report forms into drive 1.

NOTE: The T2 Report programs must be run on system disks that have been formatted to maximize disk space. Use ONLY these specially formatted disks to run the T2 programs.

(2) Insert the disk that has the JY*.DAT files into DY1: drive. In this report, the symbol '*' denotes a user-entered filename.

(3) Check the directory of the system disk. The names of the two files *.DAT and *.CON that are generated by the T2CON and JOBFIL programs have to be unique. **Note:** If necessary delete any unnecessary *.DAT and *.CON files to maximize disk space on the system disk. The file TTIO.DAT should never be deleted.

(4) Enter R T2CON- For details see T2CON.

(5) Enter R JOBFIL- For details see JOBFIL.

(6) Enter R T2FORM- For details see T2FORM.

Details:

T2CON: The T2CON program was written to store concentration data for the T2 elements determined by the JY-48P ICP.OES. The program will ask for the concentration filename in which the concentration data are going to be stored. This file will appear on the system disk as *.CON.

The program will now ask the user to enter

(1) The JY file name to start.

(2) The JY file name to end the sequence.

(3) The duplicates and/or SRM filenames if there are any.

NOTE: To ensure the proper execution of the T2FORM program, the sample identifiers for the JY data must have the form LLNNN.DAT where LL are letters and NNN are numbers. When a batch of samples are run on the JY, the sample identifiers are numbered in sequence; e.g.PW125 to PW175 inclusive for a batch of 51 samples. A batch of samples is a group of samples from one to ten different jobs. It is important that NO duplicates are allowed within the above sequence. The duplicates should be numbered with a 'D' appended to their JY filenames. For examples PW125 and PW170 will have their duplicates labelled as PW125D and PW170D respectively. SRM identifiers do not have to follow this rule. Refer to the example dialogue included with this report.

The data are stored into the concentration file *.CON (which was created at the beginning of the execution of this program) and is ready for the final reporting program T2FORM.

JOBFIL JOBFIL creates a 'sample identifier' file (file (1)) and a 'job number with geologist name' file (file (2)). Both files will be stored on the system disk with the file extension ".DAT" files must be deleted if the same filenames are going to be used again. The program will process a maximum of 10 jobs and a maximum total number of 150 samples. **Note:** Do not delete the TTIO.DAT file on the system disk under any circumstances.

The user is then requested to enter the total number of jobs to be reported. This number will be stored in the first record of file (2). Then for each job, you will be prompted to enter information in the following order:

(1) The geologist's name.

(2) The corresponding job number or date received.

(3) The corresponding sample identifiers in the order that they will appear on the report form. This also corresponds to the order in which they were processed by T2CON.

If there is a common prefix for the sample identifiers, the user is allowed to enter the prefix once prior to the entries of the sample numbers. The maximum number of characters allowed for either the prefix or the sample numbers is less than or equal to 5 (maximum number of characters for a sample identifier is 10). For example, the prefix and the sample number for the sample identifier 87AAA-0001 are 87AAA and -0001 respectively. Once the required information has been entered, the program allows the user to go back and alter any of the entered information. The total number of samples for all of the jobs to be reported is stored in the first record of file (1). Refer to the example dialogue included with this report.

T2FORM The T2FORM program produces the final T2 reports from the secondary corrected concentration data. The program will ask for the name of the file that contains the concentration data (*.CON created by the T2CON program), the file name for the sample identifiers and the file name for the geologists names and job numbers (the two *.DAT which were created by the JOBFIL program). These files should appear on the system disk as a *.CON file and two *.DAT files. The concentration data are then rounded to the nearest one ppm rock and compared with the method detection limit for each element. Any results that are less than the method detection limits are printed as the minus of the method detection limits. Results that are greater or equal to one percent are rounded to the nearest decimal with a 'P' (percentage) appended to them. The program will then print out the final concentration file. The record number (*) associated with each sample is printed out at the left of the page (refer to the example outputs).

For each job to be reported, the program will prompt for the following information:

1) The record number (*) associated with the first and last samples in the job.

2) Are there any duplicates?

If so, then enter the record numbers associated with the first and last duplicates. Changes are allowed at this point.

3) The number of T2 elements to be reported.

If less than 11 T2-elements are requested for a job, the user will be asked to enter the required number of elements for that job. If W is included in the T2 package, enter 11 for the number of T2 elements, otherwise enter 10.

4) The name of the analyst.

5) The report date.

Change the paper to 14 7/8" x 11" and position the print head at the last line position of the page. Vertical and horizontal pitches on the DEC terminal have to be changed to 6 and 8 respectively. When all this has been done, press the RETURN key and the program will printout all of the jobs on a T2 form that is ready to be reported.

AQUEOUS SAMPLES ANALYSIS PACKAGE
INDUCTIVELY COUPLED PLASMA
SOURCE EMISSION SPECTROSCOPY

Introduction:

A general introduction to the principles of ICP source emission spectroscopy is given in the Overview to Trace Element Determination by ICP Optical Emission Spectroscopy. An explanation of potential interferences and procedures for dealing with these is also presented.

The Geoscience Laboratories is able to accept aqueous samples for analysis on the JY48P ICPOES Spectrometer. No sample preparation is required and simultaneous determination of up to 36 elements is possible. The available elements are Sn, Mo, W, B, Zn, P, Pb, Co, Ba, Sc, Cr, Mg, V, Nb, Ca, Ag, Ti, Dy, Y, Eu, Sr, Gd, Ni, Ta, Mn, Fe, Si, Al, Be, Cu, Yb, Zr, Sm, La, Nd and Ce.

The method can be applied to a wide variety of aqueous samples. Data may be biased due to the presence of numerous spectral interferences. All of these interferences are quantifiable, but may degrade the determination limits. It is advisable to discuss the potential problems inherent in a specific sample matrix with the Supervisor, Spectroscopy Subsection, prior to the submission of aqueous samples.

Safety advisory:

Refer to the Trace 2 Package.

Method:

Refer to the Trace 2 Package. The one major difference between these samples and the method as described earlier is that the dissolution (digestion) technique can be ignored.

Apparatus:

Refer to the Trace 2 Package.

Productivity:

Refer to the Trace 2 Package.

Additional Notes:

Refer to the Trace 2 Package.

Reagents:

Refer to the Trace 2 Package.

Procedures:

Refer to the Trace 2 Package.

Quality Control:

Determination Limits and Ranges for Elements in Aqueous Samples

Element	Range (ppm)	Element	Range (ppm)
Sn	0.04 - 200	Mo	0.02 - 35
W	0.03 - 40	B	0.02 - 30
Zn	0.01 - 30	P*	0.30 - 5000
Pb	0.40 - 500	Gd	0.04 - 15
Co	0.01 - 3	Ni	0.02 - 35
Ba*	0.003 - 45	Ta	0.04 - 10
Sc	0.01 - 1	Mn*	0.003 - 100
Cr	0.01 - 3	Fe*	0.07 - 2800
Mg*	0.15 - 3000	Si*	1.0 - 1200
V*	0.01 - 4	Al	0.25 - 7000
Nb	0.02 - 2	Be*	0.001 - 0.1
Ca*	0.07 - 1200	Cu*	0.004 - 100
Ag	0.025 - 3	Yb*	0.002 - 0.5
Ti*	0.01 - 100	Zr	0.015 - 15
Dy	0.02 - 3	Sm	0.06 - 15
Y	0.004 - 1	La	0.025 - 7
Eu	0.005 - 1	Nd	0.15 - 30
Sr*	0.01 - 150	Ce	0.4 - 40

* These elements are routinely determined at less than optimum sensitivity due to their high natural abundances. Lower determination limits may be possible if requested.

TENTATIVE SPECTROSCOPIC ANALYIS PACKAGE (TSPA)
INDUCTIVELY COUPLED PLASMA
OPTICAL EMISSION SPECTROSCOPY

Introduction:

A general introduction to the principles of ICP optical emission spectroscopy is given in Overview to Trace Element Determination by ICP Optical Emission Spectroscopy. An explanation of potential interferences and procedures for dealing with these is given.

The Tentative SPectroscopic Analysis (TSPA) package provides semiquantitative analysis of 26 elements including Al, Ba, Be, Ca, Ce, Cr, Co, Cu, Fe, La, Pb, Mg, Mn, Mo, Ni, Nb, Nd, P, Sr, Ta, Ti, W, V, Y, Zn and Zr. Results are reported in terms of percentage concentration ranges.

Safety advisory:

Refer to the Trace 2 Package.

Method:

Refer to the Trace 2 Package.

Apparatus:

Refer to the Trace 2 Package.

Reagents:

Refer to the Trace 2 Package.

Procedures:

Refer to the Trace 2 Package.

Quality Control:

Refer to the Trace 2 Package.

Productivity:

Refer to the Trace 2 Package.

Additional Notes:

Refer to the Trace 2 Package.

APPENDIX A
GENERATION OF THE TSPA CERTIFICATES

Introduction:

A series of programs have been written to allow a user to generate signature-ready TSPA certificates and/or worksheets. There are three programs that must be run to accomplish this task: INFORM, ELEFIL and WORCER. This report describes the use of the programs.

The INFORM program sets up a client database file that can be easily updated with new information as required. Each time TSPA samples are run, new client information will be added to the database. This file will appear on the system disk as *.DAT file. In this report, the symbol '*' denotes a user-supplied file name.

The ELEFIL program allows the user to select the elements of interest. At the present time, the TSPA program for the JY48 is fixed in this regard, so this utility program need only be run once to create the necessary element data file. If the number of elements in the JY48 TSPA program is changed, this program must be run again. The element identifier file is stored on the system disk as *.DAT.

The WORCER program is used to produce the signature-ready certificates and/or worksheets.

Procedures:

1. Insert the system disk for the TSPA certificate and/or worksheet into drive 1.

NOTE: The TSPA certificate and/or worksheet program must be run on the system disks that have been formatted to maximize disk space. Use ONLY these specially formatted disks to run the TSPA programs.

2. Insert the disk that contains the data into drive 2, i.e., the original JY48 *.DAT TSPA files (in percent concentrations format).
3. Check the directory of the system disk and make sure the client information file and element identifier file are present.
4. Enter R INFORM. For details see INFORM.
5. Enter R ELEFIL. For details see ELEFIL.
6. Enter R WORCER. For details see WORCER

INFORM

The INFORM program allows a user to enter, delete, verify or save client information (names, addresses, etc.) into a *.DAT file on the system disk.

The program will first prompt for the client information file name. The first time this program is run, the file will be created on the system disk.

The program will then present the following options:

1. Verify the client information on file

2. Enter new information

3. Change information in a record

Option 1

Under option 1, the user can obtain a hardcopy of part or all of the client information on file. The program will tell the user how many clients (i.e., the total number of records) are on file and then prompt for the number of records to be printed.

If the whole file is to be displayed, then enter the total number of records on the file. If only part of the file is going to be displayed, the user will then enter in the particular record numbers of interest. The client information will be printed out and the program will terminate execution. This option should be used whenever new information has been entered since an updated hardcopy of this file is required when the WORCER program is used.

Option 2

Option 2 is run when new information is to be saved into the client information file. If the client file exists, the new information is appended. If the client file is new, then the file will be created using the name the user entered at the beginning of the program. In the case of a new file, the program will initialize the file records and print out a message to this effect. There is programmed protection against overwriting an existing file, but no protection is fool-proof, so pay close attention to any messages that may be printed out at this point in the program.

The program will then prompt for the following information:

a. Client's name?
b. Address?
c. City, province and postal code?
d. More information to be entered?

The maximum number of records in each client file is 100. The program will print out the starting record number before it prompts you for the new information so the user can act accordingly (i.e., if a client file is filled, then a new file can be started).

When no further information is to be entered, the data is written to the client file and an appropriate message is printed. The total number of clients on file will be written to the last record of the client file. The user can now produce a hardcopy of part or all of the file.

Option 3

Option 3 allows the user to modify names, addresses etc. in a particular record. The program prompts for the number of records to be altered (or ≤ 100) and then prompts for the individual record numbers. The information in these records is printed for verification. The program then prompts for the new client information as per the procedure in Option 2 and also gives the user the option to print out part or all of the client file.

ELEFIL

ELEFIL creates a *.DAT on the system disk. This file contains all the elemental identifiers associated with the JY48 TSPA analysis. The maximum number of elements allowed is 30. At present, the number of elements used for the certificate or worksheet is 27 including total radioactivity. The TSPA data from the JY48P also includes arsenic, silver and tin. These have to be included, even though they are not reported. Therefore, the total number of elements in the file is 30.

The program will prompt for a filename to store the element identifiers. **NOTE:** The element identifiers must be entered in the same order as they appear in the original JY48 data file. Once the required information has been entered, the program allows the user to correct the entered information.

WORCER

This program generates the signature-ready TSPA certificates and/or worksheets. It prompts for the names of the client information file (created with the INFORM program) and the element file name (created by the ELEFIL). The program will prompt the user to enter the total number of clients and then, for each client in turn, asks:

a. the record number corresponding to the client's name and address

b. the date the samples were received

c. the total number of samples for this client

For each sample, the program will ask for the sample identifier that is to appear on the certificate, the associated JY48 *.DAT file name and the total radioactivity for the sample.

Once the client information has been entered, the user has the option of producing the worksheet (one or two copies), the certificate or both. The program will prompt the user to change vertical and horizontal pitches on the DEC terminal to 6 and 12 respectively.

The user is also prompted to line up the print head to the appropriate position and insert carbon paper in the case of the TSPA certificate. **NOTE:** If both the worksheet and certificate are required, the worksheet is printed first, then, after changing paper, the corresponding certificate is printed.

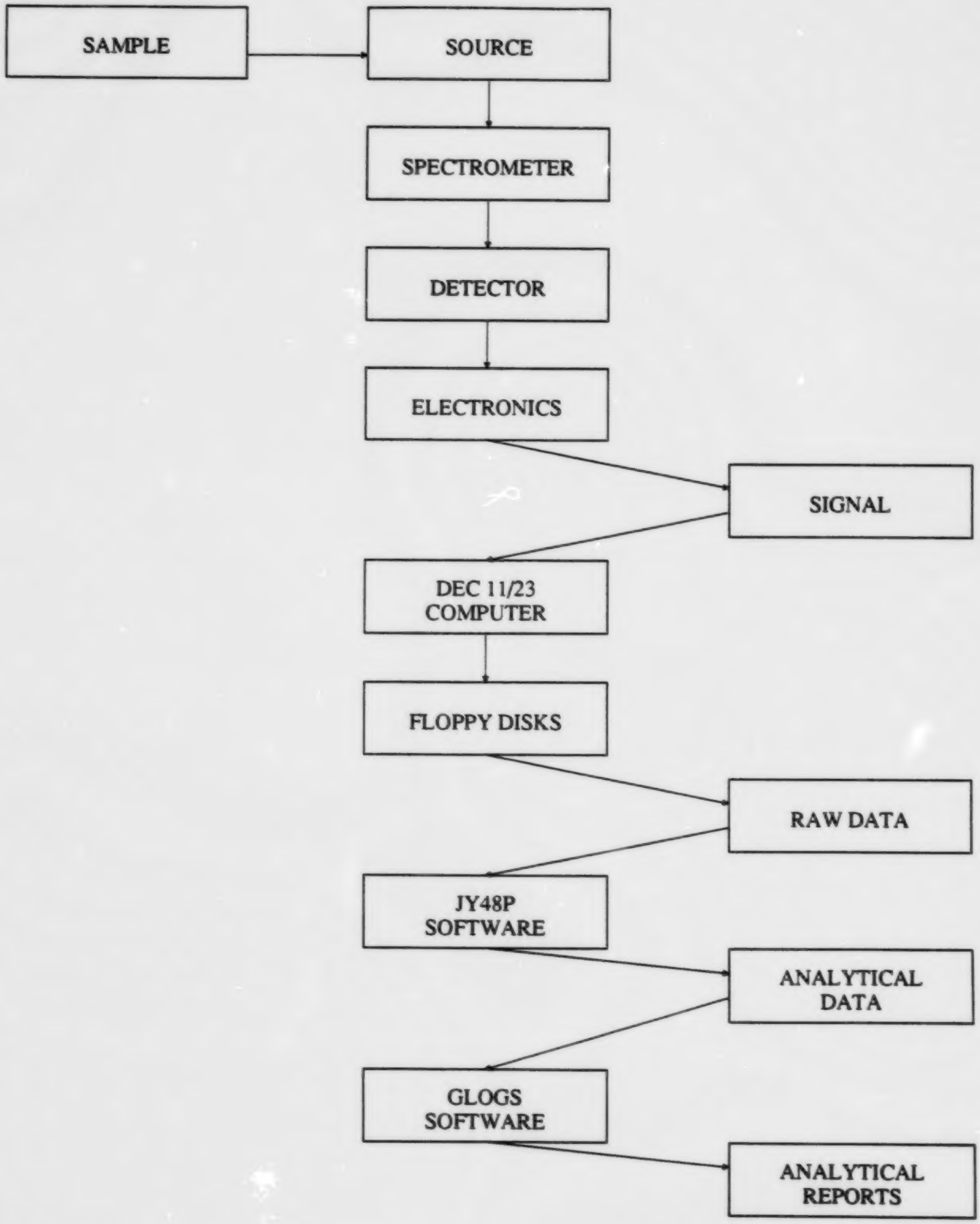
SAMPLE
SOURCE
SPECTROMETER
DETECTOR
ELECTRONICS
SIGNAL
DEC 11/23 COMPUTER
FLOPPY DISKS
RAW DATA
JY48P SOFTWARE
ANALYTICAL DATA
GLOGS SOFTWARE
ANALYTICAL REPORTS

Figure ICP1. Schematic Diagram.

SAMPLE PREPARATION FOR THE T4 AND T5 ICP-MS PACKAGES

Introduction:

The ICP-MS technique is not well suited to the direct analysis of solid geological samples because wet chemical preparation procedures are preferred to decompose the samples. The techniques outlined below are suitable for the determination of the following elements in most rocks:

- Y and the lanthanide elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) i.e., the complete T4 package.
- Hf, Ta i.e., part of the T5 package (Th, U, Sn, Pb and Tl are also included in the T5 package, but the HF stabilization technique has not been validated for the determination of these elements).
- Rb, Cs, Nb, Zr and Sr. The concentrations of these elements are generally determined by XRF as part of T3 package. The concentrations of Nb and Sr can also be determined by ICP-OES. Analysis for these elements by ICP-MS is primarily intended for those situations where use of the other two techniques is inappropriate (e.g., small sample sizes, efficient use of resources or determination limit requirements).

The technique below calls for the addition of a small amount of hydrofluoric acid to the final solution. This addition keeps traces of Hf, Ta, Nb and Zr in solution while avoiding the precipitation of the lanthanides as fluorides. If analysis for Hf, Ta, Nb and Zr is not required, then it is not necessary to add HF to the final solution.

Safety advisory:

1. Two different acid mixtures are used for sample preparation. For safety reasons, the composition of each must be recorded on the dispensing bottles.

2. When using HF, wear glasses and gloves, and be extremely careful. More information on HF is available in the Geoscience Laboratories' Safety Manual.

3. Nitric acid, hydrochloric acid, and perchloric acid are corrosive substances. Wear protective clothing and exercise caution when handling these substances. Additional information on perchloric acid is available on pages EA2-1 and EA2-2.

Apparatus:

- 50 ml Teflon beakers
- plastic pipettes
- two 500 ml graduated plastic acid-dispensing bottles with graduated dispensing reservoir (to be used for the T4A and T4B acid mixtures) containing HF or $HClO_4$.
- two 500 ml low actinic glass acid-dispensing bottles for dispensing concentrated HNO_3 and HCl
- one 500 ml low actinic glass acid-dispensing bottle with calibrated dispensing barrel for use with the Ru/Re internal standard mixture

Reagents:

- Hydrofluoric acid, HF, 48% - 51%
- Hydrochloric acid, HCl, 36% - 38%
- Nitric acid, HNO_3, 69% - 71%
- Perchloric acid, $HClO_4$, 62% - 70%

Procedure:

1. Reagent Preparation

Two acid mixtures are used for sample preparation. The composition of each must be recorded on the plastic dispensing bottles. The dispensers are also labeled T4A and T4B.

1.1. T4A solution is prepared by measuring concentrated 400 ml HF, 40 ml HCl, and 40 ml $HClO_4$ and mixing them in a 500 ml graduated, plastic dispensing bottle. When preparing these solutions, always add the acid to water.

1.2. T4B solution is prepared by measuring 380 ml deionized distilled water, 70 ml HCl, and 30 ml $HClO_4$ and mixing them in a 500 ml graduated plastic dispensing bottle.

2. Standard Preparation

2.1.1. Pipette 5 ml of 1000 g/ml Ru, followed by 5 ml of 1000 g/ml Re into a 500 ml volumetric flask. Make to volume with 10% HNO_3. Use class A volumetric glassware.

2.1.2. Transfer to a 500 ml glass dispensing bottle.

2.1.3. Verify that the Ru and Re concentrations in the old and new standard solutions are the same. Comparison is done by dispensing (using the 500 ml internal standard dispensing bottle) 1 ml of the standard into a 100 ml class A volumetric flask and making to volume with 10% HNO_3. This solution is then be compared against the old standard by examining the signal trace for each standard (and each analyte) on the ICP-MS using the SPEC_DIS program. You should not be able to discern any differences between the signal traces for the two standard solutions.

3. Sample Dissolution

3.1.1 Weigh 200 mg of sample into a Teflon beaker and add 15 ml of T4A solution. Using the T4A solution, wash down the sides of the beaker.

3.1.2. Prepare and carry at least 2 blanks and 2 aliquots of the digestion control material through the entire procedure (see Quality Control Section).

3.1.3. Place sample and acid on a hotplate which has been set to 120°C. Leave overnight. Contamination of the sample can occur from debris falling from structural members of the fumehood above the hotplate, so be sure that all necessary precautions have been taken to avoid this.

3.1.4. The next morning, remove the beaker from the hotplate and gently tap the beaker to dislodge the cake.

3.1.5. Add 15 ml of the T4B solution, replace on hotplate and leave overnight again.

3.1.6. To the hot dry sample cake, add 8 drops of concentrated HCl, allow to cool for about 1 minute and then add 1 ml of concentrated HNO_3 and swirl the solution gently.

3.1.7. Using the plastic dispensing pipette, add 4 drops of concentrated HF and swirl the solution gently.

3.1.8. Add approximately 15 ml of deionized distilled water and replace the beaker on the hotplate and reduce the volume to about 10 ml. THE SOLUTION MUST NOT BE ALLOWED TO GO TO DRYNESS. If it does, the aliquot must be discarded and the procedure repeated.

3.1.9. Remove the beaker from the hotplate and cool to room temperature.

3.1.10. If the samples are not going to be transferred within a few hours, add about 25 ml 10% HNO_3.

3.1.11. Transfer 1.0 ml of the internal standard solution to a clean 100 ml volumetric flask. Using 10% HNO_3, transfer the contents of the beaker to this flask and make to mark with 10% HNO_3.

3.1.12. Use Parafilm to stopper the flask and shake thoroughly.

3.1.13. Transfer an aliquot of the solution to a 15 ml snap-cap polystyrene test-tube.

3.1.14. The solutions are ready for determination by ICP-MS.

Quality Control:

The sample digestion procedure is monitored by including reagent blanks and in-house reference materials in the batch of client samples. Three hotplates are used for the sample digestion. Each hotplate can accommodate 20 of the 50 ml Teflon beakers.

When a batch of samples is prepared, include one reagent blank and one in-house reference material on each hotplate used. A bottle (Bottle #55) of the in-house basalt reference material (a basalt collected by P. C. Lightfoot in 1988) has been characterized for quality control purposes for the following analytes: Rb, Sr, Y, Zr, Nb, Cs, the lanthanides (except Pm), Hf and Ta.

Since about 60% of the samples listed on the PETROCH database are basalts, KIWI is appropriate reference material. During the certification of this reference material, three people prepared a total of 24 aliquots and the solutions were analyzed once by the procedures outlined in this manual (Table MS1). Means and associated standard deviations were calculated from these data and the values are used to monitor the digestion step of the T4 and T5 procedures.

TABLE MS1. DIGESTION CONTROL DATA (IN-HOUSE REFERENCE BASALT (1988) MATERIAL, BOTTLE #55, N=24)

Element	Mean µg /g	Std. Dev.
Rb	14.374	0.348
Sr	307.3	6.64
Zr	173.84	4.431
Nb	13.6	0.20
Cs	0.229	0.009
Hf	4.578	0.145
Ta	0.823	0.028
Y	25.025	0.662
La	21.342	0.655
Ce	50.273	1.484
Pr	6.104	0.17
Nd	27.247	0.65
Sm	6.105	0.156
Eu	1.873	0.045
Gd	5.658	0.152
Tb	0.838	0.023
Dy	5.037	0.20
Ho	0.994	0.022
Er	2.581	0.090
Tm	0.363	0.014
Yb	2.366	0.072
Lu	0.351	0.015

Reagent blanks from each batch must always be checked. However, after three years of using the T4 procedure, a reagent blank (RBLK) problem has yet to be encountered for Y and the REE, although Zr has a substantial reagent blank contamination (typically 2 ppm in the rock) as does Hf (typically 0.05 ppm in the rock). These RBLK values for Zr and Hf are established by using the Elan 'QUANT' program and the run protocol:

> 10% HNO_3, RBLK1, 10% HNO_3, RBLK2, ...,
> 10% HNO_3, 80 ppb calibration standard

Results are calculated manually. The average analyte signal measured for the 10% HNO_3 solutions, which bracket the RBLK, is subtracted from the RBLK solution signal. A sensitivity factor is calculated from 80 ppb/cps_{net} where cps_{net} is the analyte signal corrected for the 10% HNO_3 signal obtained immediately prior to the 80 ppb calibration solution standard.

The instrument must have warmed-up sufficiently so that signal drift is minimal (approximately 3/4 of an hour).

The digestion-control standard data for a particular batch is compared against the above values by calculating the number of standard deviations the control solution data differ from the mean. These calculations are printed at the end of the interim report produced by the Apple II concentration calibration/calculation software. This interim report is filed along with the original bench sheets for the job. The run number associated with the data is also included on the bench sheets. The run numbers on a particular data disk are written on the disk label. The run numbers on a particular data disk can also be identified by using the Apple II utility program 'FIXRUNQUE'.

With all this information, data can be retrieved as required. The reagent blank data for Zr and Hf and the average value used in calculating the results for reporting are hand written on the bench sheets.

Productivity:

Sixty samples (2 RBLK, 2 digestion check preps and 16 samples per hot plate) can be prepared in three days. With assistance, two batches per week could be prepared if the first batch is started on Monday. Assistance during the final transfer step is required if a second batch of samples is to be started on the Wednesday of the work week.

Additional Notes:

1. Concerning the final steps of the digestion procedure (addition of 8 drops concentrated HCl followed by 1 ml concentrated HNO_3). It is **imperative** that the HCl be added first. Failure to do so will result in irreproducible Hf, Ta, Nb and Zr analyses and the samples will have to be reprepared from the beginning.

2. The gloves have a talcum coating on the inside. Wash the outside of the gloves before tranferring samples to avoid getting talcum from inside the gloves in the sample.

3. The beakers are cleaned in tap-water solution of "Sparkleen". Rinse this soap solution with hot water. Otherwise, a thin soap film is left on the beaker.

4. The Ru/Re dispensing bottle has a screw-on cap which connects the bottle with the dispensing device. **DO NOT SCREW** the cap on too tightly, otherwise, a vacuum is produced and air bubbles end up in the dispensing barrel. Occasionally unscrew the cap to avoid this.

5. **Maintenance** - Work areas in and near the fumehood and work bench should be cleaned whenever required. The fumehood has internal plumbing for washing down the stacks and the inaccessible walls of the fumehood. This should be used at the finish of each batch. Bytac protective Teflon covering has been installed and should be wet mopped between batches.

THE ELAN-250

Introduction:

This document is intended for use as a bench procedure for the routine operation of the Sciex 250 Elan Inductively Coupled Plasma Mass spectrometer.

Method:

The instrumental method consists of the following procedures:

1. Instrument start-up
2. Mass calibration
3. Signal optimization
4. Setting up the run
5. Performing analysis
6. Analyzing the run
7. Performing calculations
8. Instrument shutdown - normal operation
9. Instrument shutdown - emergency procedure

Procedures:

1. Instrument Start-up

Become familiar with the location of all switches and controls on the instrument before operation. Many of the steps require a sequence to be performed quickly. If things go wrong, don't panic, but move immediately. If you are not confident about any operation do not start the procedure, or abort the procedure and seek assistance.

1.1.1. The outer sleeve of the torch should extend 37 mm past the tip of the aerosol injector (i.e., long torch).

1.1.2. The torch should be positioned in the work coil so that the distance between the aerosol injector and the bottom turn of the load coil is 2 mm.

1.1.3. The torch stand should be positioned so that when it is at the extreme end of its travel towards the torch, the injector tube is 43 mm away from the sampling orifice and the top turn of the load coil is 23 mm from the sampling orifice. After this distance has been checked ("by eye") move the box away from the sampling orifice until it rests against the back stop. The box will be returned to the stop position after the plasma is ignited.

1.1.4. Visually ensure that the load-coil centre-tap solder join is intact and the interface/torch cooling water is on.

1.2. Starting The Computer

1.2.1. Activate the printer using the toggle switch at the back left-hand corner.

1.2.2. Activate the Envision monitor/terminal using the switch at the back left-hand corner.

1.2.3. Wait 10 - 15 seconds.

1.2.4. Activate the Elan computer using the switch labelled 'POWER' on the face of the computer.

1.2.5. Wait 30 seconds.

1.2.6. Press the switch labelled 'RESET' on the Elan computer panel.

1.2.7. Wait (3-4 minutes) until the following message appears at the top of the monitor:

```
"XXXX Files     XXXXX Blocks     XXXX Free"
```

If there are more than 3000 files, or less than 700 free, DO NOT PROCEED. Contact the person responsible for the ELAN.

NOTE: The Elan software relies on the use of a color coded numeric keyboard. In the procedures described here, the following short forms for references to operator responses using this keypad; the keys are numbered left to right 1,2, and 3, G = Grey, R = Red, Y = Yellow, B = Blue and Gn = Green.

1.2.8. At the "Login: " prompt type Elan [R]. Then type in Y [R] to the prompt "Does the printer need initialization (y/n)".

1.2.9. Press B3. The screen should now display text titled "ECL Commands". Make sure caps-lock is off. The computer is now operational.

1.3. Starting the Plasma Source

1.3.1. Turn on the RF Generator by depressing the CKTS push button.

1.3.2. Turn the reflected power switch on the APCS-3 panel to OFF.

1.3.3. Turn the power pot on the R.F. generator to a setting of about 8.2.

1.3.4. Check that the voltage to the channel electron multiplier (CEM) detector is switched off by checking that the left-hand toggle switch on the fourth board from the top in the signal and ion lens electronics rack is set to the left.

NOTE: One lead of the R10 resistor on the CEM board has been disconnected. This is to ensure that the CEM on/off toggle switch will always turn off volts to the detector independent of the computer status.

1.3.5. If the lens/quadrupole power supplies are not energized, replace relay K1. Check that the yellow relay below K1 is seated properly.

NOTE: This yellow relay controls the valves between the mechanical pump and the mass spectrometer chamber. Improperly seated, this relay could leave one of the valves open and the mass spectrometer will not get out of stage 1 pumpdown.

1.3.6. **IMPORTANT: Turn on the interface and load coil water supply located at the sink beside the distilled deionized water-still in the ICP lab (far right tap).**

1.3.7. Ensure that the torch stand has been moved away from the interface plate and is resting against the back stop.

1.3.8. Turn on the argon gas supply and nebulize deionized water (plasma gas 16 l/min, auxilliary 2.2 l/min, nebulizer gas 1.0 l/min) and allow the system to flush for 3-4 minutes.

1.3.9. Plug in the autosampler.

1.3.10. Turn off the nebulizer gas flow using the needle valve control knob. When the nebulizer pressure gauge registers minimum, bleed in about 0.05 l/min.

1.3.11. Set the drum capacitor (toggle switch on the front upper left corner of the torch-box) to MANUAL and adjust the drum capacitor reading to 82 using the white buttons located to the left of the toggle switch.

1.3.12. After the start-up value has reached 82, set the toggle switch to AUTOMATIC.

1.3.13. Set the RF torch-box power pot to zero (fully counter clockwise) and push the RF ON button.

1.3.14. Rotate the RF torch-box power dial in a clockwise direction so that 0.5 kW of forward power is indicated on the forward power meter. Maintain contact with the power dial; it may be necessary to adjust it for more or less power during the ensuing operations. Activate the tesla coil by depressing the white "ICP IGNITE" button located on the torch stand control panel. It may be necessary to adjust the forward power up to initiate the plasma or down to stop arcing.

NOTE: Arcing from the coil to the torch (accompanied by the green Cu emission, sparks and the sound of RF arcing) occurs occasionally, (particularly when 1.4 kW power are used instead of 0.5 kW). If this happens, QUICKLY rotate the power knob COUNTER-CLOCKWISE i.e., to OFF. Push the RF POWER OFF button. A check should then be made to ensure the load coil centre tap solder join is intact and the interface/torch cooling water is on.

1.3.15. At this point, the plasma should light. If it does not ignite after a few seconds, press the RF POWER OFF button and consult the senior technician or Supervisor.

1.3.16. Rotate the power pot to select a forward power setting of 1.5 kW, as indicated on the Forward Power Meter.

1.3.17. The following operations should be performed quickly:

- depress the 'Operation' button ON.
- switch the 'RF Reflected' toggle switch ON.
- turn the power knob to 'MAX' (fully clockwise).
- open the nebulizer gas line via the needle value to 1.0 l/min.

1.3.18. Wait for the interface gate to begin dropping, then move the torch stand forward (up to the interface plate), until it reaches the end of its travel. Lock it in place using black knobs.

1.3.19. Place the ultraviolet shield in place.

1.3.20. Check the mass spectrometer vacuum (8-12 x 10^{6} torr) and temperature (17-19°K). If the gauges do not indicate these values consult the senior technician or Supervisor.

1.3.21. Turn on the CEM.

1.4. Daily Checkout Routine:

The operating conditions used for the daily checkout and sample analysis are listed in Table MS2. Lens voltage settings are not fixed. Consult with a senior technician or Supervisor if there are any questions on this matter.

TABLE MS2. ICP-MS OPERATING CONDITIONS

Plasma Conditions	
Torch	Extended outer sleeve style
RF power	1.5 kW
Reflected power	<5 W
Aux. flow (intermediate)	2.2 l/min
Nebulizerflow	1.0 l/min
Plasma gas flow (outer)	16 l/min
Solution uptake rate	0.85 ml/min

1.4.1. Allow the plasma, mass spectrometer and detector to warm up for about 20 minutes.

1.4.2. Ensure that all instrument operating parameters are set to the values indicated in Table MS2.

2. Mass Calibration

This procedure must be carried out at the beginning of every work day. It updates the mass calibration, and tests instrument sensitivity by providing intensity data which can be compared with standard (previously acquired) data.

2.1.1. Enter SPEC DIS [R]. The first page of the Spectrum Display program will show up on the screen. The cursor can be moved through the various fields by entering [R].

2.1.2. Nebulize a solution containing 80 ppb REEA.

2.1.3. Press R1. The second page of the Spectrum Display software, (Measurement Settings), will appear.

2.1.4. Move the cursor and change the displayed fields to match those listed in Table MS3.

2.1.5. Press R1 again. The Mass Selection page should appear.

NOTE: The Elan software relies on the use of a color coded numeric keyboard. In the procedures described here, the following short forms for references to operator responses using this keypad: the keys are numbered left to right 1,2, and 3, G = Grey, R = Red, Y = Yellow, B = Blue and Gn = Green.

Scanning:

2.1.6. Enter 139 [R] ... Enter 139 [R] again. The Elan will scan over this mass range (the 139La peak).

2.1.7. Press G3 to start the scan.

2.1.8. Press [R] in response to the prompt "Press [R] or Abort to continue".

2.1.9. Press G1 to get into Graphics mode.

2.1.10. Press and hold the 'FUNCT' key down. While this key is depressed, press Gn3. This will engage the crosshair markers.

2.1.11. Continue holding the 'FUNCT' key and press Y3. Move the vertical crosshair to the middle of the peak.

2.1.12. Continue holding the 'FUNCT' key and press R2. Move the horizontal crosshair to the apex of the peak.

2.1.13. Release the 'FUNCT' and the R2 keys.

2.1.14. Press R1 to zoom in on the image and use 'FUNCT' R2, and 'FUNCT' Y3 to adjust the markers so that they intersect at the centre of the peak.

2.1.15. Press R3 to zoom back to original image size. Record the peak position (to 2 decimal places).

2.1.16. Press and hold the 'FUNCT' key down. While this key is depressed, press Gn3 twice. This should remove the crosshair markers.

2.1.17. Press G1 to get out of Graphics mode.

2.1.18. Press Gn3 to stop scanning (a bell should sound).

2.1.19. Press Gn1 to get the Mass Scan Range selection screen.

2.1.20. Repeat the above scan procedure for ^{89}Y, ^{175}Lu, ^{151}Eu. Record all four observed masses.

2.1.21. Press Gn1 three times to return to the "ECL Commands screen".

Mass Calibration

2.1.22. Enter Mcal [R]

2.1.23. Enter REEMCC [R]

2.1.24. Enter m [R]

2.1.25. Press G1 to get to the mass-entry screen.

2.1.26. Enter the observed mass for Y [R].

2.1.27. Enter the observed mass for La [R].

2.1.28. Enter the observed mass for Eu [R].

2.1.29. Enter the observed mass for Lu [R].

2.1.30. Press G3 to obtain print out of the day's mass calibration. These are filed for 1 - 2 months.

2.1.31. Press Gn1 to get back to the first screen of mass calibration.

2.1.32. Press G3 to save the new mass calibration table.

2.1.33. Press Gn1 to get back to the ECL command screen.

3. Signal Optimization

If the sampler and/or skimmer has been removed, then the signals must be optimized. The operating conditions and measurement parameters are listed in Tables MS2 and MS3.

TABLE MS3. MEASUREMENT PARAMETERS

Measurement mode	Sequential, 1 point per analyte peak
Measurement time	0.5 s/point
No. integrations	6
Resolution	0.9 amu at 10% valley

Analyte	Mass (daltons)	Oxide/isobar int.*
Y	89	
Zr	90	
Ru	99	
La	139	
Ce	140	
Pr	141	
Nd	143	
Sm	147	
Eu	151	^{135}BaO
Tb	159	^{143}NdO
Gd	160	^{144}NdO, ^{160}Dy
Dy	163	^{147}SmO
Ho	165	^{149}SmO
Er	167	
Tm	169	
Yb	174	^{158}GdO
Lu	175	
Re	185	

* This column represents the oxide and isobaric corrections considered significant. Other species may be formed but their contributions are considered negligible.

3.1.1. Ensure the plasma, mass spectrometer, and detector have warmed-up for about 20 minutes.

3.1.2. Ensure that all instrument operating parameters are set to the values indicated in Tables MS2 and MS3.

3.1.3. Set the Photon Stop and Plate digipots to zero.

3.1.4. Set the Einzel and Barrel digipots to 70 and 50 respectively.

3.1.5. Select the "Mulelem" program (ECL command). Select the measurement conditions to monitor the following masses ^{111}Cd and ^{187}Os. Use 1/2 s/point, 1 point/peak. Toggle the isobaric correction for ^{187}Os off.

3.1.6. While monitoring the ^{189}Os background signal, increase the Plate digipot setting until just before the background signal starts to rise.

3.1.7. Monitor the ^{139}La signal while nebulizing a 80 ppb REEA solution.

3.1.8. If the copper sampler and skimmer have just been cleaned, the 1000 ppm Ca solution must be nebulized for about 10 minutes to deposit a layer of Ca oxide on sampler and skimmer to protect them from inadvertent exposure to hydrochloric acid.

3.1.9. Monitor the signal from 80 ppb Y, La, and Lu (REEA solution) and adjust the Barrel voltage until the Y and La signal are about equal. This adjustment is normally very small. The Y signal must not be significantly lower (maximum 10% difference) than the La signal.

NOTE: The La counts should be about 70 to 110 kHz depending on the condition of the sampler and skimmer. A newly Ca conditioned sampler and skimmer give 70-80 kHz. During sample analysis, as material is deposited on the sampler and skimmer, the counts typically drift up over part or all of the REE mass range.

NOTE: Using kHz as a unit for an ion signal is a good way of reminding one that the number which is presented as the intensity is a measure of frequency (i.e., counts per second) with which ions strike the detector. For example, the noise power spectrum of an instrument can be experimentally determined, possibly giving insight to the source of signal noise in the instrument and perhaps uncovering ways to improve analytical precision.

3.1.10. Adjust the Barrel lens so that the ^{89}Y and ^{175}Lu signals are maximized.

NOTE: This procedure typically results in the signal strengths being skewed in favour of the lighter REE. Adjusting the Barrel and Einzel voltages to make the ^{89}Y and ^{175}Lu signal approximately equal generally results in an unacceptable overall loss of signal across the mass region of interest.

3.1.11. If the observed intensities are lower than expected, check the torch position.

4. Setting Up the Run

4.1.1. Load the autosampler according to the following protocol:

Run Protocol

Sample solutions are run with the autosampler in batches using the following scheme:

ACDBLK	10% nitric acid
INTERFERENCE STANDARDS	REEA/REEB
DRIFTSTD	REESTD
JUNK	
CHK	
7-10 samples	
CHK	
7-10 samples.....	
CHK	
DRIFTSTD	
BLK	reagent blank

NOTE: The sample IDs ACDBLK and BLK must be used. CHK is the within-run control standard whose values are established against those of an SRM. Currently a rock composite solution has been calibrated for REE against BHVO-1 and is used as the CHK solution. JUNK is a sample primarily used to minimize memory effects from the drift standards.

4.1.2. Position the first sample in the run so that it is in front of the sample sipper.

4.1.3. Initiate analysis as described below.

5. Performing Analysis

Quantitative analysis is performed with the aid of two computers: the instrument computer and a microcomputer (Apple IIe). The Apple computer collects and stores the raw intensities during analysis. At the conclusion of the run, it processes the data to determine final concentrations. The operation of these computers is described below.

This procedure consists of two parts;

1. Setting up the run i.e., entering sample id's, dilution factors etc.,
2. Running the samples.

Setting up the run

5.1.1. Confirm that the "ECL Command" display is on the screen. If not press Gn2 until the display no longer changes and then press B3.

5.1.2. Enter QUANT [R]. The cursor can be moved to the various fields by using [R].

5.1.3. Type the name of the appropriate parameter set followed by [R]. (NOTE: The Calibration Field must ALWAYS show "STD_"). If it doesn't then change it to the correct value.

5.1.4. Enter [R] twice.

5.1.5. Enter a run number followed by [R].

5.1.6. Enter a run description followed by [R].

5.1.7. Enter n [R] twice.

5.1.8. Enter s [R].

5.1.9. Press G1 to get to the Sample Entry screen.

5.1.10. Enter sample identification and description (usually the OGS job number). Use [R] to select fields.

5.1.11. Press G1 to store the sample information.

5.1.12. Continue entering sample information and pressing G1 until all samples identifiers have been entered.

5.1.13. When finished press Gn1 to get back to the first screen of 'QUANT'.

6. Analysing the Run

6.1.1. Use [R] to move the cursor to the "Run Mode" field and enter a [R] to indicate that the autosampler is to be used.

6.1.2. Place the Elan Apple System Disk in the left-hand drive.

6.1.3. Place the Intensity Data Disk (appropriate to the analysis to be performed) in the right-hand drive.

6.1.4. Activate the monitor (front top right-hand corner of the video terminal).

6.1.5. Activate the computer (back lower left-hand corner). After about 30 seconds, the display will show the Elan Apple main menu.

6.1.6. Select option 1. This will initiate the intensity data collection program.

6.1.7. Respond to the first prompt by entering the appropriate parameter set name.

6.1.8. The program will prompt for; 1) Run ID, 2) Autosampler (y/n), 3) Number of tubes in the run. Enter this information following each entry with [R].

At this point, the screen will display the ordinal number associated with the sample/tube position in the run. The record number into which the data will be written in the Apple disk file will also be displayed.

NOTE: The Apple II keyboard will be 'live' at this time. The Apple cannot distinguish between a keyboard entry from data comming from the Elan. Consequently, inadvertent keyboard entry will corrupt the data and probably cause termination of the program. So don't touch the Apple keyboard.

6.1.9. After information has been entered, return to the Elan and press G1 to begin the analysis.

The program running on the Apple II will monitor the data coming from the Elan. Upon completion of the set of samples, the Elan will return to the first screen of the 'QUANT' program. The Apple will require additional input.

6.1.10. Respond to the following Apple prompts:

- Do more analysis using the same parameter set?

If answer is no then:

- Do analysis using a different parameter set?

If answer is still no, the program returns to the main menu.
If answer is yes, the program will proceed and will ask for parameter set name etc., as before.

NOTE: Be certain to place appropriate data disk (for new parameter set) in the right-hand drive BEFORE ENTERING THE NEW PARAMETER SET NAME.

7. Performing Calculations

There are two calculation algorithms in use. An internal standard technique has been developed for Y and the Rare Earth Elements (REE), Hf, Ta, Nb, Rb, Cs, Sr, and Zr. All other analyses utilize external calibration with signal drift compensation (linear interpolation).

7.1.1. Select option 2 from the Apple main menu. The 'CONCAL' menu will be displayed. Place the intensity data disk in the right-hand drive.

7.1.2. Select the appropriate calculation algorithm.

7.1.3. Enter the slot number for the printer card.

7.1.4. Enter the parameter set name for the set used to collect the data.

7.1.5. After 30 seconds, the program will display the identifiers of unprocessed runs and prompt for the run number to be processed. Select the desired run number.

7.1.6. The program will prompt for the filename to be used to store instrument and preparation QC data. Enter the appropriate filenames. If this function is not being used enter '$' to bypass these functions.

7.1.7. The program will read the intensity data. Wait until the program is finished doing this and has displayed the prompt requesting a "Default Dilution Factor". Enter the factor.

7.1.8. The program will prompt for any factors that are different from the default. Enter these factors.

The program will perform the intensity to concentration calculations. No additional input is required until after the final results have been printed.

7.1.9. The program will prompt for the number of the instrument QC solution identifiers and their positions in the run. Enter the correct information.

The program will calculate and produce a report summarizing the instrument QC data. This information is presented as the difference between the observed and the expected values divided by the standard deviation associated with the expected value. If the error is normally distributed, then 66% of the results should be between 0 and one standard deviation. Less than 0.5% of the results will be greater than 3 standard deviations when there is no determinate error associated with the measurement. If such an occurrence is observed, then there is good reason to believe that the measurement is biased. A run (or data between check samples) will be rejected if more than two of the check samples lie outside 3 standard deviations.

The program will calculate and produce a report summarizing the preparation QC data. This information is presented in a manner similar to that produced for the instrument QC. The program will then ask whether the concentration data is to be stored. Respond appropriately. If the data is not to be stored, the program will return to the 'CONCAL' main menu.

If the data is to be stored, three options will be presented: 1) Routine Sample Data Storage 2) International Reference Material 3) In-house Reference Material. Some or all of these options may be used for one set of data.

7.1.10. The program will display each sample-identifier and prompt for the proper run-identifier. Routine sample data should be stored using the four digit run-number assigned by the lab (i.e., job number).

7.1.11. The program will prompt the operator to place the appropriate data disk in the right-hand drive. Place the disk in the correct drive.

When all data has been stored, the program returns to the main 'CONCAL' menu.

8. Instrument Shut-Down - Normal Operation

8.1.1. Turn off the detector.

8.1.2. Unlock the torch-stand.

8.1.3. Depress the 'Operation' button OFF and, as the gate begins to rise, steadily move the torch stand away from the interface plate.

8.1.4. Slowly, but steadily, decrease the forward power until the plasma extinguishes and then depress the 'RF OFF' button.

8.1.5. Turn off the water to the interface and the load coil.

8.1.6. Allow the RF generator to cool for 10 minutes before shutting it off.

8.1.7. Exit the ELAN control programs (software shutdown).

8.1.8. Turn off the 'Envision' terminal, printer, depress the 'DISCS' button and turn the computer power off.

NOTE: This must be done at the end of every day otherwise there is a chance of damage to the computer.

9. Instrument Shut-down - Emergency Shutdown

Emergency situations previously encountered include broken water/gas lines and grinding noises from the cryopump.

9.1.1. Depress the big RED button on the front of the torch- stand or RF generator.

9.1.2. Depress the 'Operation' button OFF.

9.1.3. Turn off the detector.

9.1.4. Turn off the water to the interface and the load coil.

In cases where the situation is considered serious, quickly shut down the power to the instrument using the breaker switch located outside room 1019 (Panel C, Switch #2) or turn the power button OFF located on the front panel of the instrument.

NOTE: When powering back up, the emergency 'lock' clasp on the red button must be released or power will not be restored using the normal start-up sequence. Push the red button in and turn slightly - it will pop back out into the normal position.

Temporary Loss of Cooling Water: Occasionally the building water supply is turned off. Since the cryopump must have cooling water to run, the instrument is best put into cryoclean (cryopump is not required) for the duration of the interrupted service. A full pumpdown from atmospheric will be required after (2-3 hours).

TRACE 4 (T4) ELEMENTS
INDUCTIVELY COUPLED PLASMA SOURCE MASS SPECTROSCOSPY

Introduction:

This suite of elements comprises a geochemically coherent group that has many geological applications. Minerals such as apatite, zircon, monazite and other accessory phases usually concentrate the REE in a sample, although these elements can substitute for Ca and Sr in rock-forming minerals such as feldspar, amphibole or pyroxene. The REE are typically reported normalized to a chondritic meteorite composition on a semi-log diagram which is automatically included in the T4 data report.

The REE provide evidence concerning the formation of the solar system, the evolution of the crust from the mantle, generation of magma within the crust. All such data are used in petrogenetic modelling and to understand ore formation and the interplay of fluids of various compositions with pre-existing rocks. Also, the radioactive decay of La and Sm to Ce and Nd (respectively) over geologically significant time periods can yield further insights into crustal processes.

The speed, precision and elemental coverage of the determination of REE abundances by ICP-MS is unequalled by any other analytical technique. However, although isotopic ratios can be determined by ICP-MS, the precision on the isotopic ratios is not competitive with thermal ionization mass spectrometry (TIMS), except for screening purposes.

The Trace 4 (T4) package consists of the elements listed in Table MS4, along with the typical determination limit, optimum range and precision quoted as the 95% Confidence Limit (ppm) for a value at 10 times the determination limit.

Safety advisory:

There are a number of potential safety hazards associated with the use of this equipment. UNTRAINED OPERATORS MUST NOT USE THE EQUIPMENT. The OGS ICP-MS has had many modifications and consequently starting procedures are very different from a standard factory delivered instrument.

TABLE MS4. DETERMINATION LIMITS AND PRECISION FOR THE T4 ELEMENTS

Element	Determination Limit	Optimum Range (ppm)	Precision
Y	0.02	0.02-200	0.02
La	0.05	0.05-200	0.05
Ce	0.05	0.05-300	0.05
Pr	0.05	0.05-200	0.05
Nd	0.18	0.18-200	0.18
Sm	0.15	0.15-100	0.15
Eu	0.07	0.07-20	0.07
Gd	0.14	0.14-100	0.14
Tb	0.03	0.03-20	0.03
Dy	0.13	0.13-20	0.13
Ho	0.03	0.03-20	0.03
Er	0.10	0.10-20	0.10
Tm	0.03	0.03-20	0.03
Yb	0.11	0.11-20	0.11
Lu	0.04	0.04-20	0.04

(Chondrite plots are automatically included with T4 Data Reports)

There are five types of hazard associated with this apparatus; electrical, radiation, high temperature, noxious gases and physical hazard.

1. Electrical hazards can be encountered in three areas; the plasma power generator, the plasma torch compartment, the spectrometer tank compartment. Such hazards are also associated with various peripheral equipment like pumps, autosamplers and other special apparatus which may be set up to facilitate the analysis. The RF power generator is of particular concern because high voltages are retained on capacitors even when the power has been completely disconnected from the instrument. DO NOT ATTEMPT TO GAIN ENTRY TO THE RF POWER GENERATOR WITHOUT PROPER TRAINING. Other areas are protected by interlocks. DO NOT OVERRIDE INTERLOCKS.

2. High voltages should be marked stating the approximate voltage. Wear safety glasses where sparks or arcing may occur. Remove rings and metal watchbands when working with circuits or control devices. Never handle electrical equipment with wet or perspiring hands. Some high voltage danger points are:

    - Transformer terminals
    - Rectifier-tube plate caps
    - Filter capacitor terminals
    - Filter choke
    - RF tuning capacitors and coils
    - Fuse panels

3. Two types of electromagnetic radiation are of concern, radio frequency and ultraviolet. Radio frequency radiation has no known teratogenic effect, but can cause somatic damage. Such radiation could affect eyesight as the eye fluids will absorb the radiation which causes a damaging increase in pressure within the eye. Ensure that the plasma torch compartment is well shielded by inspecting the viewing and access ports to make sure that the RF radiation cannot escape. The 50 ohm coaxial cable should be inspected to ensure that it is a tight fit and that no corrosion has occurred at the connecting points on both the instrument and on the plasma power generator, (EXPERIENCED TECHNOLOGISTS ONLY!). Ultraviolet radiation is emitted by the plasma. THE PLASMA SHOULD NEVER BE VIEWED DIRECTLY. Even light from the plasma which is reflected from the source housing has a high level of ultraviolet radiation and direct viewing of this light should be avoided. If it is necessary to view the unshielded plasma, wear fully sealed No. 12 welders goggles.

4. The interlocks protecting the plasma should never be overridden. The torch itself can become quite hot and sufficient time should be allowed, after extinguishing the plasma, before disassembling the torch for routine inspection and cleaning. The plasma power tube runs at about 300°C and should be cooled at least 20 minutes prior to shutting the generator down at the end of the day or for inspection.

5. The exhaust gases from both the plasma compartment and the generator can be a source of both heat and noxious fumes. Both beryllium (a vesicant) and ozone are emitted from the generator.

    The exhaust from the plasma can contain toxic materials from the samples. THEREFORE, THE EXHAUST FROM BOTH THE GENERATOR AND THE PLASMA MUST BE VENTED FROM THE ROOM AT ALL TIMES. Remember to check the damper positions to ensure that sufficient exhaust velocity is being maintained.

6. Physical hazards can be encountered when moving or working around bottled gases. Exercise appropriate caution: secure the cylinders, use the valve caps, use properly designed carts to move the cylinders, use appropriate footwear, etc.

Method:

The method consists of the following techniques:

1. Acid digestion of the rock sample (see sample preparation - page EA19-1)
2. Determination by ICP-MS
3. Calculation of final results using (a) an internal standard or (b) from external calibration data

Apparatus:

- Inductively coupled plasma source-mass spectrometer: Perkin-Elmer Sciex ELAN 250
- Ultra-violet shield
- Microcomputer: Apple IIe with dual floppy disk drives and Epson FX printer

Reagents:

- Purified Argon gas
- Distilled deionized water
- Single element 1000 ppm stock solutions of Y, La, Ce, Nd, Pr, Sm, Eu, Gd, Dy, Yb, Ru and Re obtained from Spex Industries (Metuchen NJ)

Procedures:

1. Reagent and Standard Preparation

1.1.1. 200 ml of 1000 ppm single element stock solutions of Tb, Ho Er, Tm and Lu prepared by dissolving the appropriate amount of rare earth oxide powder (obtained from Alpha Products, Danvers, MA) in about 2 ml of concentrated HNO_3 and 6 to 10 drops of concentrated HCl.

1.1.2. For all serial dilution operations described below, use 10% HNO_3 (v/v) for the diluent.

1.2. 200 ml of a 100 ppm multielement standard (called REEA') containing Y, La, Pr, Nd, Sm, Eu and Yb prepared by serial dilution of the 1000 ppm single element standards.

1.3. 200 ml of a 100 ppm multielement standard (called REEA') containing Ce and Lu is prepared by serial dilution of the appropriate 1000 ppm single element standards.

1.4. 200 ml of a 100 ppm multielement standard (called REEB) containing Gd, Dy, Tb, Ho, Er and Tm is prepared by serial dilution of the appropriate 1000 ppm single element standards.

1.5. 200 ml of a 100 ppm solution containing Ru and Re is prepared by serial dilution of the appropriate 1000 ppm single element standards.

1.6. 200 ml of a 10 ppm solution containing Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu (called REEA') is prepared by serial dilution of the 100 ppm solutions REEA' and REEA''.

1.7. The REESTD calibration standard (containing Y, the REE, Ru and Re) is prepared by serial of the appropriate 10 ppm calibration standards.

1.8. The REEB and REEA' interference solutions are prepared by weighing 0.200 g of the appropriate 100 ppm stock solution, transferring to a 250 ml volumetric and making up to volume.

1.9. The 2 ppm Ba interference solution is prepared by weighing 0.50 g of 1000 ppm Ba stock solution and transferring to a 250 ml volumetric.

1.10. Instrument control solution identified as CHK2 was prepared by collecting the remaining solution after analysis until about 3 liters was collected. The solution was allowed to sit for about two weeks and then filtered through a 45 micron filter.

2. Measurement of Analyte Concentration

The operation of the Elan 250, and the measurement of the analyte concentration is outlined quite extensively on pages EA19-5 to EA19-12.

3. Performing Calculations

There are two calculation algorithms in use. An internal standard technique has been developed for Y and the Rare Earth Elements (REE), Hf, Ta, Nb, Rb, Cs, Sr, and Zr. All other analyses utilize external calibration with signal drift compensation (linear interpolation).

3.1. Select option 2 from the Apple II main menu. The 'CONCAL' menu will be displayed. Place the intensity data disk in the right-hand drive.

3.2. Select the appropriate calculation algorithm.

3.3. Enter the slot number for the printer card.

3.4. Enter the parameter set name for the set used to collect the data.

3.5. After 30 seconds or so, the program will display the identifiers of all the runs saved to disk and prompt for the run number to be processed. Select the desired run number.

3.6. The program will prompt for the filename to be used to store instrument and preparation of QC data. Enter the appropriate filenames. If this function is not being used, enter '$' to bypass these functions.

3.7. The program will read the intensity data. Wait until the program is finished doing this and has displayed the prompt requesting a "Default Dilution Factor". Enter the factor.

3.8. The program will prompt for any factors that are different from the default. Enter these factors. The program will perform the intensity-to-concentration calculations. No additional input is required until the final results are printed.

3.9. The program will prompt for the number of the instrument QC solutions that were run and their positions in the run. Enter the correct information.

The program will calculate and produce a report summarizing the instrument QC data. This information is presented as the difference between the observed and the expected values divided by the standard deviation associated with the expected value. If the error is normally distributed, then 66% of the results should be between 0 and one standard deviation. Less than 0.5% of the results will be greater than 3 standard deviations when there is no analytical bias associated with the measurement. Thus if such an occurrence is observed, there is good reason to believe that the measurement is biased. A run (or data between check samples) will be rejected if more than two of the check samples lie outside 3 standard deviations.

The program will calculate and produce a report summarizing the preparation QC data. This information is presented in a manner similar to that produced for the instrument QC.

The program will ask whether the concentration data are to be stored. Respond appropriately. If the data are not to be stored the program will return to the 'CONCAL' main menu.

If the data are to be stored, four options will be presented: 1) Routine Sample Data Storage 2) International Reference Material 3) Inhouse Reference Material 4) Exit Menu. Some or all of these options may be used for a set of data.

3.10. The program will display each sample identifier and prompt for the proper run identifier. Routine sample data should be stored using the four digit run number assigned by the lab (job number).

3.11. The program will prompt the operator to place the appropriate data disk in the right-hand drive. Place the disk in the correct drive.

When all data has been stored the program returns to the main 'CONCAL' menu.

Quality Control:

Precision: The CHK2 solution is used for instrument quality control purposes. The following table lists the means and associated standard deviations (established over a 1 month period) (n=50). These values are used by the QC functions of the Apple II software.

TABLE MS5. COMPOSITION OF CHK2.

Element	Mean (ug/g)	Std. Dev (n-1)
Y	18.32	0.479
La	20.535	0.422
Ce	44.164	1.14
Pr	5.013	0.147
Nd	19.347	0.535
Sm	3.962	0.128
Eu	1.121	0.038
Gd	3.629	0.118
Tb	0.552	0.022
Dy	3.447	0.123
Ho	0.703	0.031
Er	2.017	0.089
Tm	0.284	0.018
Yb	1.892	0.075
Lu	0.279	0.016

The instrument check solution was run in batches of international reference materials used in the development of the current ICP-MS T4/T5 method. Accuracy is assured in two ways: (1) by using international reference materials and (2) by matrix effect experimentation. The mean values established in this way for the CHK2 solution can be used to assess accuracy. Determination for a wider range of international reference materials (and a larger number of analytes) has been carried out (in press). For research grade jobs appropriate reference materials are run (e.g., SY-2, MRG-1, AC-E). Accuracy is about ± 5%.

Quality assurance:

The digestion and instrument control data for a particular batch are compared with the above values by calculating the number of standard deviations the control solution data differ from the mean. These calculations are printed at the end of the interim report produced by the Apple concentration calibration/calculation software. This interim report is filed along with the original bench sheets for the job. The run number associated with the data is also included on the bench sheets.

The run numbers on a particular data disk are written on the disk label. The run numbers on a particular data disk can also be identified by using the Apple utility program 'FIXRUNQUE'. With all this information, data can be retrieved as required.

Productivity:

Ideally, a technician should be able to complete about 60 solutions per day. Data reduction and reporting are not included.

Additional Notes:

1. If a clean sampler and skimmer are being used, a 1000 ppm Ca solution must be nebulized to protect them. This Ca standard must be prepared from the pure Johnson Matthey $CaCO_3$ powder. The appropriate weight of $CaCO_3$ is dissolved in a minimum volume of concentrated HNO_3 and then made up to volume with distilled deionized water.

   If work has been done in the vacuum chamber or if a new sampler or skimmer is being used for the first time, use appropriate lens optimization procedures (Doherty, 1989).

   If work has been done on the interface plates, **it is critical that the plates are centered properly on the vacuum port. The validity of the Ru-Re internal standard scheme depends on this.**

2. Under no circumstances should the deposits on the shadow stop (at the base of the skimmer) be removed as instrument drift will become uncontrollable. It takes about five working days nebulizing 1000 ppm Ca almost continuously to build up the required electrically insulating layer.

3. The air filters at the base of the RF generator and the filters at the head of the Elan (computer end) should be cleaned as required (about every 2-3 months).

4. The mechanical pump oil and alumina balls should be changed about every 5 to 7 weeks.

5. Samplers and skimmers should be cleaned at the end of every second work day. See senior staff if you have never done this before.

6. Empty the slops buckets (located behind the Elan) every three days.

Bibliography:

Doherty, W., 1989, Spectrochimica Acta, Vol. 44B, page 263.

THE TRACE 5 (T5) PACKAGE INDUCTIVELY COUPLED PLASMA SOURCE MASS SPECTROSCOPY

Introduction:

This suite of elements (Hf, Ta, Th, U; options: Pb, Sn, Tl) has been traditionally difficult to determine in geological materials because the host minerals are often refractory (difficult to dissolve and treat analytically). Futhermore, these elements usually occur in discrete accessory mineral phases thus meaning special attention must be paid to sample collection and preparation. Finally, these elements are usually found only at trace levels in most geological materials. ICP-MS provides the low determination limits required by geologists.

Elements in the T5 package have varied geological significance and, although determined as a group, these elements are not used as a single suite. Ta and Hf, found in rock-forming and accessory minerals, are used extensively to characterize the tectonic setting of basalt and granite. Ta, U, Sn, Th are used to monitor or evaluate processes that control the formation and differentiation of magma within magma chambers. They are also used to discern the possible ore potential in granitic rocks. Pb is incorporated into either galena (PbS) as a major constituent or at trace levels into potassium feldspars (common in granites). Because three Pb isotopes are produced by the radioactive decay of U or Th, the assessment of the amount of lead present in a sample can be a preselection criteria for geochronology samples. Tl is a rare element that is often associated with Au, Ag and PGE minerals. Other elements such as Rb, Cs, Sr, Zr, and Nb can be determined in the T5 package.

Safety advisory:

Refer to the Safety Advisory Section in the Trace 4 elements page EA19-13.

Method:

The method is similar to that used for the Trace 4 elements, page EA19-14.

Apparatus:

Refer to the Trace 4 method.

TABLE MS6. DETERMINATION LIMITS AND PRECISION FOR TRACE ELEMENTS (T5)

Element	Determination Limit (ppm)	Optimum Range (ppm)	Precision*
Hf	0.05	0.20 - 100	0.05
Ta	0.05	0.05 - 20	0.05
Th	0.10	0.10 - 100	0.10
U	0.10	0.10 - 100	0.10
Options			
Pb	0.10	0.10 - 100	0.10
Sn	0.50	0.50 - 100	0.50
Tl	0.10	0.10 - 100	0.10
Rb)	Under Development		
Cs)			
Sr)			
Zr)			
Nb)			

* Precision is quoted as the 95% Confidence Limit (µg/g) for a value at 10x the determination limit (i.e. absolute, not relative).

Reagents:

Refer to the Trace 4 method.

Procedures:

Refer to the Trace 4 method.

Quality Control:

Refer to the Trace 4 method.

Table MS7 contains the data for the instrument check solution. The validation of the current ICP-MS method for the other T5 elements is in progress.

TABLE MS7. COMPOSITION OF T5 CHECK SOLUTION

Element	Mean (ppm)	Std. Dev.
Rb	41.406	0.958
Sr	306.34	6.507
Zr	94.86	2.146
Nb	7.691	0.187
Cs	1.349	0.036
Hf	2.479	0.081
Ta	0.349	0.012

Accuracy is about 5%.

Productivity:

A technician should be able to complete 60 samples a day. This does not include data reduction and reporting time.

Additional Notes:

1. The T5 package requires three separate solution with the T5 elements separated as follows:

    a. Hf, Ta, Sr, Zr, Nb, Rb, Cs
    b. Pb, Th, U, Tl
    c. Sn

    The 80 ppb working solution is prepared by serial dilution of the 1000 ppm stock solutions.

2. The Ru-Re calibration scheme is used for Rb, Cs, Nb, Sr, Zr, Hf and Ta. All others use the external calibration procedure. Thus, separate runs on the Elan 250 are required to accomplish a full T5 analysis.

3. Sn fusion solutions received from the Chemistry Subsection are further diluted by a factor of 5 for a final dilution factor of 2500.

DETERMINATION OF THE RARE EARTH ELEMENTS (La, Ce, Nd, Sm, Eu, Yb, Lu), THORIUM, TANTALUM, HAFNIUM, URANIUM AND SCANDIUM BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

Introduction:

Instrumental neutron activation analysis (INAA) provides non-destructive determination of the REE, Th, Ta, Hf, U and Sc. These elements are extremely useful as tracers in a wide variety of geological processes (refer to Volume I Chapter 16).

An advantage with this method is that it does not involve dissolution. A disadvantage is that it does not allow for the determination of all rare earth elements.

Safety advisory:

1. Sample containers should be air-tight and handled with extreme caution to avoid the leakage of radioactive rock dust after the samples are removed from the reactor and attached to the aluminium counting plates with masking tape.

2. Avoid irradiating samples which become very 'hot' during long irradiations. If the samples are not common silicate rocks, then check to ensure that long-lived radioisotopes are not produced during irradiation. Tantalum ores are an example of samples which become 'hot'.

3. Ensure that samples >1% in volatile elements such as chlorine are not introduced into the reactor.

Users must take an official University of Toronto safety course before commencing work, and the user must be signed-in to the reactor facility in the presence of the supervising staff (R.G.V. Hancock).

Method:

The method consists of the following techniques:

1. Sample preparation - bagging and accurate weighing of the samples and standards

2. Irradiation of samples - placing them into the nuclear reactor for a 16 hour time period

3. Measuring the concentration - counting the 'cooled' samples after 7 and 40 days, with on-line data reduction

4. Calculation of the results based on a comparison of counts from the samples with counts from standards

Apparatus:

- Bag sealing unit
- Slowpoke II nuclear reactor
- Gamma counter and multichannel analyzer equipped with computer for on-line data reduction

Reagents:

None required.

Procedure:

1. Sample preparation

A wide range of geological samples can be analyzed by neutron activation, and there are many different preparation techniques. The following procedure may be followed:

1.1. The weight of the rock powder is recorded to four decimal places. Pulverized rock powder weighing 300-400 mg is sealed in plastic using a bag-sealing unit. The container is marked using a indelible marker pen. UTB-1 is used to make up a reference standard, and either WHIN SILL (the Open University irradiation standard) or BHVO-1 are used to monitor quality within and between batches of samples.

1.2. Up to twenty small 'baggies' are placed in each cylinder for irradiation. Normally, there is no need for flux corrections when irradiation is completed in a small reactor of the SLOWPOKE type.

1.3. Samples are irradiated for 16 hours, and counted 7 and 40 days after they are removed from the reactor.

2. Determination of element concentrations

The sample is affixed to the center of an aluminium plate so that it is flat and free of wrinkles. The plate is inserted into a rack on the nose of the detector. Data are acquired using a Canberra multi-channel analyser (MCA) with the spectral regions of interest defined in Table NAA1.

Each sample is counted for 5000 or more live seconds to achieve a 2σ error of 10%, or better, for the peaks of interest. Dead time must be <15% or an alternative sample with lower dead time should be counted first.

The multi-channel analyzer is equipped with two detectors (ADC#1 and ADC#2) and collects counts simultaneously from both detectors. Peaks may be examined and regions of interest established whilst data acquisition continues.

Quality Control:

UTB-1 (University of Toronto Basalt Standard) is used in establishing a primary calibration. Secondary standards are used to ensure precision and accuracy are within acceptable limits (Refer to NAA2); various external standards are available for this purpose.

Productivity:

This technique is not automated, and is extremely labour intensive. It may take about eight days over a 60 day period to produce data for 50 samples.

Bibliography:

Frogatt, P., (unpublished), Analyzing for Rare Earth Elements by Neutron Activation at the University of Toronto Slowpoke Reactor.

TABLE NAA1. TABLE OF ELEMENTS AND INTERFERENCES PEAKS FOR INAA COUNTING

7 day counts			40 day counts		
Element	**Peak (eV)**	**Interferences**	**Element**	**Peak (eV)**	**Interferences**
Ho	80.6	TEMP	Ta*	67.8	
Nd	91.0	Ba @ 92.3 & possible Br	Tm	84.3	Ta @ 84.6
Sm	103.2	U, Th	Eu	122.0	Ba @ 124
U	106.4		Ce	145.4	Th
Mo	140.3		Ba	216.0	Tb @ 215.6
Lu	208.3	U @ 209.7	Tb*	298.6	Th @ 300
Ba*	216.0	Th @ 215.6	Th*	311.9	
Yb	282.6		Cr	320.1	
Tb	298.6	Th @ 300 (poor)	Hf	482.0	
Th	311.9		Cs	795.8	
Yb*	396.1	Th	Ni	810.8	
Au	411.8		Tb	879.3	
As	559.1		Sc	889.3	
La	815.6		Fe	1099.3	
Sc	889.3		Zn	1115.5	Tb
Rb	1076.6		Ta	1221.3	
Fe	1099.3		Co	1332.5	
La*	1596.2		Eu*	1408.1	

* Preferred peak for most rocks

TABLE NAA2. ANALYTICAL DATA FOR ROCK STANDARDS DETERMINED BY INAA DURING A ROUTINE ANALYTICAL SCHEME

Element	Mean UTB1 (ppm)	σ	Expected Value (ppm)	Mean WHIN SILL	σ	Epected Value (ppm)
Th	4.21	0.06	(4.3)	2.75	0.26	(3.1)
Ta	0.96	0.06	(1.02)	1.6	0.9	(1.26)
Hf	5.06	0.96	(4.6)	4.92	0.48	(4.9)
U	1.02	0.18	(1.0)	0.45	0.14	(0.90)
La	26.4	1.6	(26.7)	24.7	0.5	(22.5)
Ce	62.1	2.8	(60.5)	60.4	3.8	(57.5)
Nd	33.6	2.0	(32.0)	28.4	5.2	(32.9)
Sm	7.98	0.18	(8.0)	7.02	0.26	(7.3)
Eu	2.30	0.22	(2.4)	2.04	0.10	(2.3)
Yb	4.05	0.42	(4.0)	2.5	10.14	(2.54)
Lu	0.64	0.06	(0.58)	0.35	0.02	(0.39)
Sc	40.0	1.3	n.d.	30.4	0.8	n.d.

n.d. not determined

DETERMINATION OF GOLD, PLATINUM AND PALLADIUM GRAPHITE FURNACE ATOMIC ABSORPTION METHOD

Introduction:

A renewed interest in the search for deposits of Au, Pt and Pd has been stimulated by recent economic and political events. This, in turn, has led to improvements in the methodologies by which laboratories determine the levels of these elements in geochemical samples.

It is well known that Au, Pt and Pd are distributed in rocks in a heterogeneous manner, occurring as discrete particles and minerals and existing in solid solutions in sulfides, silicates, and spinels. Because of this so-called 'nugget effect', a minimum of 10 g of rock powder is used.

There has been a significant increase in the number of analytical techniques used to determine Au, Pt and Pd in the past decade. Of these techniques, there is a general consensus that graphite furnace atomic absorption spectrophotometry is well suited in the routine determination of these elements.

The natural abundance level for platinum is about 0.05 ppb, which is approximately eighty-fold lower than for gold. Platinum tends be be slightly more abundant than palladium.

Gold, platinum and palladium are determined in geological materials by graphite furnace atomic absorption spectrophotometry utilizing an autosampling system.

These elements are concentrated into a silver bead of approximately 15 mg by the classical lead fire-assay method (page M14-5). Dissolution of the silver bead is accomplished with nitric acid in a 10 x 75 mm test tube placed in an aluminum block and set on a hotplate. The silver is precipitated as the chloride with hydrochloric acid whereby the gold, platinum and palladium are dissolved in the aqua regia.

The acid mixture is diluted with distilled water, mixed and the AgCl allowed to settle on the bottom of the test tube. An aliquot of the supernatant liquid is atomized in a graphite furnace and the atomic absorption signal observed as a recorder trace.

Safety advisory:

1. The method involves the use of specific acids to dissolve the silver bead. Personnel should review the MSDS sheets for these acids prior to use.

Method:

This method consists of the following techniques:

1. Preparation of silver bead (sample fusion and extraction)

2. Sample decomposition by acid digestion

3. Measurement using graphite furnace atomic absorption

4. Calculation of Au, Pt, and Pd concentrations based on a calibration curve produced from known standard solutions

Apparatus:

- Perkin Elmer model 603 atomic absorption spectrophotometer equipped with a model 56 chart recorder.
- HGA 500 graphite furnace and programmer with microcomputer controlled power supply.
- AS-1 auto sampler - includes sample table with provision for 30 samples; sampling dipper assembly with separate electronic control unit containing precision pumps for sampling and rinsing.
- Test tubes, borosilicate, 10 X 75 mm
- Aluminum heating block

Reagents:

- Matrix acid mixture
- Nitric acid, HNO_3, (1:3)
- Hydrochloric acid, HCl, (1:3)
- 1000 ppm Au - such as supplied by Fisher Scientific Company (gold chloride in distilled water)
- 100 ppm Au standard solution
- 10 ppm Au standard solution
- 1000 ppm Pt - such as supplied by BDH Chemical
- 100 ppm Pt standard solution
- 10 ppm Pt standard solution
- 1000 ppm Pd - such as supplied by BDH Chemical

- 100 ppm Pd standard solution
- 10 ppm Pd standard solution
- Working Standard Solutions

Procedures:

1. Reagent preparation

1.1. Nitric acid (1:3) - To a 500 ml volumetric flask containing 200 ml of distilled water add 125 ml of concentrated nitric acid. Cool and make to volume with distilled water.

1.2. Hydrochloric acid (1:3) - To a 500 ml volumetric flask containing 200 ml of distilled water add 125 ml of concentrated hydrochloric acid. Cool and make to volume with distilled water.

1.3. Matrix acid mixture - To a 1000 ml volumetric flask containing approximately 500 ml of distilled water, add 62.5 ml of concentrated nitric acid and 62.5 ml of concentrated hydrochloric acid. Cool and make to volume with distilled water.

2. Standard Au, Pt, and Pd solution preparation

2.1. 100 ppm Au solution - Pipet 20 ml of 1000 ppm Au into a 200 ml volumetric flask and make to volume with 0.5 N HCl.

2.2. 10 ppm Au solution - Pipet 20 ml of 100 ppm Au into a 200 ml volumetric flask and make to volume with 0.5 N HCl.

2.3. 100 ppm Pt solution - Pipet 20 ml of 1000 ppm Pt into a 200 ml volumetric flask and make to volume with matrix acid mixture.

2.4. 10 ppm Pt solution - Pipet 20 ml of 100 ppm Pt into a 200 ml volumetric flask and make to volume with matrix acid mixture.

2.5. 100 ppm Pd solution - Pipet 20 ml of 1000 ppm Pd into a 200 ml volumetric flask and make to volume with matrix acid mixture.

2.6. 10 ppm Pd solution - Pipet 20 ml of 100 ppm Pd into a 200 ml volumetric flask and make to volume with matrix acid mixture.

2.7. Working standard solutions - Prepare 0.5, 0.10, 0.20 and 0.30 ppm Au, Pt and Pd solutions by adding 0.5, 1.0, 2.0 and 3.0 ml of 10 ppm Au, Pt or Pd solution with a 10 ml microburette to 100 ml volumetric flasks. Make to volume with the matrix acid mixture.

3. Sample decomposition (acid digestion)

3.1. Add by microburette 0.5 ml of (1:3) nitric acid to a 10 x 75 mm test tube containing the silver bead obtained from the fire-assay technique.

3.2. After dissolution of the silver, 0.5 ml of (1:3) hydrochloric acid is added and the contents mixed. The AgCl precipitate is digested in the test tube and placed in an aluminum block on a hot plate.

3.3. Heat until the supernatant solution is clear and the AgCl has coagulated as a 'lump' on the bottom of the test tube.

NOTE: Do not heat so long that a loss of volume occurs through evaporation.

3.4. To the acid mixture, add 1.0 ml of distilled water using a microburette. The test tube is then shaken and placed in the aluminum block to cool.

3.5. Transfer a portion of the supernatant solution to a sample cup to determine gold, platinum and palladium.

4. Measurement of Au, Pt and Pd concentrations

Set up the Perkin-Elmer 603 atomic absorption spectrophotometer equipped with an HGA 500 Programmer and Graphite Furnace and utilizing the AS-1 auto sampling system according to the procedure described in the manufacturer's operation manual.

The atomic absorption signal is measured with a Perkin-Elmer Model 56 recorder. The instrument parameters for each element are listed in the following table.

Instrument Parameters

	Au	Pt	Pd
Lamp Current	8 mA	12 mA	16 mA
Wavelength	242.8nm	265.9nm	247.6nm
Slit Width (setting)	0.7nm(4)	0.7nm(4)	0.2nm(3)
Background Corrector	On	On	On

The following parameters are common for Au,Pt and Pd:

Water Coolant rate	2.5 l/min
Sample Volume	20 µl
Recorder Power	Servo
Chart Speed	40 mm/min
Range	5 mv (for 0.05 to 0.30 ppm Au and Pd) 2 mv (for < 0.05 ppm Au and 0.05 to 0.20 ppm Pd) 1 mv (for 0.05 to 0.20 ppm Pt and < 0.05 ppm Pd)

Graphite furnace program steps

A. Drying Temperature	120°C
Ramp time	10 sec
Hold time	25 sec
B. Charting Temperature	800°C
Ramp time	15 sec
Hold time	15 sec
C. Atomization Temperature	2700°C
Ramp time*	0 sec **
Hold time	5 sec

Enter - 5 and press REC key, READ key and INT. GAS key

* Must be entered to automatically apply maximum power heating. Calibration of the optical temperature control is necessary.

** For Pt use 5 sec.

5. Calculation of the results

The concentrations of gold, platinum and palladium in the sample solution are read with the aid of a calibration graph. The net concentration is obtained by subtracting the average overall-blank value. The concentration in the sample is calculated according to the formula:

$$M = \frac{CV}{W} x\ 1000$$

where :

M = ppb of Au, Pt or Pd in rock

C = net concentration of Au, Pt or Pd in g/ml in solution

V = Volume in ml of the sample solution (usually 2ml), and

W = weight of sample in grams (usually 10 g)

Quality Control:

The optimum working range for Au is 2 to 40 ppb, and 1 to 40 ppb for Pt and Pd (in rock).

The determination limit is 2 ppb Au in rock, and 1 ppb for Pt or Pd.

The estimated precision, at 95% confidence limit (2σ), for a value at 10 times the determination limit, is ± 5 ppb for Au and ± 3 ppb for Pt and Pd (relative).

Accuracy is comparable to precision based on data collected from standard reference materials.

Productivity:

A technician should be able to complete 20 samples per day if there are no usually high concentrations.

Additional Notes:

1. Standards must be prepared with the same acid concentrations contained in the samples, that is, nitric acid (1:15) and hydrochloric (1:15).
2. All dilutions must be made with an acid mixture containing these same concentrations.
3. Standards should be prepared every 2 weeks and stored in polypropylene containers.
4. Concentrations of 50 ppm of platinum, palladium, and silver have no interfering effect on a gold absorbance represented by 0.2 ppm.
5. Concentrations of 50 ppm silver, gold and platinum have no interferring effect on a palladium absorbance represented by 0.2 ppm.
6. The following observations on the absorbance of a 0.2 ppm Pt solution are:

   50 ppm Ag reduced the absorbance by 5%,
   50 ppm Au and 5 ppm Pd had no effect, and
   50 ppm Pd reduced the peak absorbance by 10%

Bibliography:

"Analytical Methods for Atomic Absorption Spectroscopy Using the HGA Graphite Furnace", Revised March 1977, Perkin Elmer Corporation, Norwalk, Connecticut U.S.A.

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DETERMINATION OF GOLD IN NATURAL WATERS SOLVENT EXTRACTION AND ELECTROTHERMAL ATOMIZATION METHOD

Introduction:

A renewed interest in the search for deposits of gold has been stimulated by recent economic and political events. This, in turn, has led to improvements in the methodologies by which laboratories determine the levels of these elements in geochemical samples.

The determination of gold in water is based on the method described by McHugh (1984) in which a one liter sample is evaporated to dryness, the residue is dissolved in bromine-hydrobromic acid, gold is extracted into methyl-isobutyl ketone, and determined by graphite furnace atomic absorption spectrophotometry (GFAAS).

The gold content in the MIBK portion (or in the 1 liter of water) is calculated based on the concentration of gold in MIBK and the volume of MIBK. The extraction procedure includes back washing with dilute HBr to remove unwanted iron in the MIBK phase, thereby optimizing the accuracy of measurement.

Safety advisory:

1. Reagent preparation and sample extractions are to be done in a fume hood to avoid inhaling and exposure to MIBK vapor and acid fumes.

2. Great care should be exercised in pipetting bromine, to avoid dripping or spilling of the obnoxious liquid. (Never pipet by mouth, always use a pipette bulb)

Method:

The method consists of the following techniques:

1. Extraction and preconcentration of the gold

2. Measurement of the gold absorption signal by GFAAS

3. Calculation of the gold concentration based on a calibration curve produced from known standard solutions

Apparatus:

- Perkin Elmer Model 603 atomic absorption spectrophotometer equipped with a model 56 chart recorder.
- HGA 500 graphite furnace and programmer with microcomputer controlled power supply.
- AS-1 autosampler
- Pyrolytically coated graphite tubes
- Hot plate
- Glass beakers, 400 ml
- Glass filtering funnels and Whatman No. 40 filter paper
- Glass separatory funnels, 125 ml
- Glass test tubes, 10 X 75 mm

Reagents:

- Hydrobromic acid, HBr, 48%
- Hydrochloric acid, HCl, 38%
- Nitric acid, HNO_3, 70%
- Bromine
- 0.5% bromine in hydrobromic acid
- Cleaning solution
- Methyl-isobutyl ketone, MIBK
- 0.1N HBr solution
- 5% (v/v) Br_2-HCl solution
- 1000 ppm Au standard solution - (gold chloride in distilled water)
- 1 ppm Au in 8% HCl solution
- 100 ng Au/ml in 8% HCl solution
- 5 ng Au/ml in 0.5% bromine in hydrobromic acid

Procedures:

1. Reagent preparation

1.1. 0.5% bromine in hydrobromic acid - pipet 1 ml of bromine into a 200 ml volumetric flask and make to volume with hydrobromic acid.

1.2. 0.1N HBr solution - Add 6 ml HBr to 500 ml of distilled water in a one liter separatory funnel. Equilibrate with 25 ml of MIBK. Discard excess MIBK. Store in a stoppered glass container.

1.3. 5% (v/v) Br_2-HCl solution - pipet 10 ml of bromine into a 200 ml glass volumetric flask and make to volume with concentrated hydrochloric acid.

1.4. Cleaning solution - mix nitric acid, hydrobromic acid and distilled water in the ratio of 1:3:10.

2. Standard Au solution preparation

2.1. 1 ppm Au in 8% HCl - prepare accurately by serial dilution of the 1000 ppm Au standard solution with 8% HCl.

2.2. 100 ng/ml of Au in 8% HCl - pipet 5 ml aliquot of the 1 ppm Au solution into a 50 ml glass volumetric flask and make to volume with 8% HCl.

2.3. 5 ng/ml of Au in 0.5% bromine in hydrobromic acid - pipet 2.5 ml aliquot of the 100 ng/ml Au solution into a 50 ml glass volumetric flask. Make to volume with 0.5% bromine in hydrobromic acid. (This solution is stable for 1 month).

3. Extraction and preconcentration of the gold

3.1. Add 10 ml of 5% (v/v) Br_2-HCl solution to the water sample in the polyethylene container to desorb Au from the container walls. Allow to stand for 2 days with occasional shaking.

3.2. Filter one liter of water sample using a Whatman No. 40 filter paper.

3.3. Evaporate the water sample in aliquots on a hot plate using a 400 ml beaker. It will take about 15 hours to evaporate a one liter sample to near dryness. Do not allow the sample to boil, particularily toward the end of the evaporation.

3.4. Add 7 ml 0.5% bromine in hydrobromic acid from a burette.

3.5. Warm gently and allow to stand for 15 minutes.

3.6. Transfer the solution to a clean 125 ml separatory funnel.

3.7. Rinse the beaker with 7 ml distilled water added from a burette and add the rinsings to the separatory funnel.

3.8. Add 2 ml MIBK from a 10 ml microburette to the separatory funnel.

3.9. Shake for five minutes.

3.10. Allow layers to separate (about 15 minutes) and drain off the aqueous layer (centrifuge if emulsion forms).

3.11. Add 8 ml 0.1N hydrobromic acid solution from a burette.

3.12. Shake for one minute, allow to stand for 15 minutes and drain off aqueous layer.

3.13. Transfer the MIBK extractant solution to a test tube using a disposable pipette.

3.14. Determine absorbance by graphite furnace AAS technique.

3.15. Prepare 5, 10, and 20 ng standards daily by pipetting 1, 2, and 4 ml of 5 ng/ml Au in 0.5% Br_2-HBr solution into three separatory funnels followed by 6, 5, and 3 ml of 0.5% Br_2-HBr solution respectively. Add 7 ml of distilled water to each of the funnels. Continue as from step 3.8 to 3.14.

4. Measurement of Au concentration

4.1. Set-up the Perkin-Elmer 603 atomic absorption spectrophotometer equipped with a HGA 500 programmer and graphite furnace and utilizing the AS-1 auto sampler according to the procedure described in the manufacturer's operation manual. The atomic absorption signal is measured as peak height with a Perkin-Elmer Model 56 chart recorder. The instrument parameters are listed in the following table.

Instrument Parameters

Wavelength	242.8 nm
Lamp Current	8 mA
Slit with setting	4 (0.7 nm)
Deuterium arc back ground corrector	on
Signal	absorbance

Recorder

Power	servo
Chart Speed	40 mm/min.
Range	1 mV

P-E Model HGA 500 graphite furnace and AS-1 auto sampler

Purge gas	argon
Sample Volume	20 µl
Rinsings	water

Graphite furnace program steps

A. Drying Step	
Temperature	120°C
Ramp time	10 sec
Hold time	10 sec
B. Charring Step	
Temperature	800°C
Ramp time	10 sec
Hold time	5 sec
C. Atomization Step	
Temperature	2700°C
Ramp time	3 sec
Hold time	3 sec

Enter -5 and press REC key, READ key, and INT FLOW key.

4.2. Record the absorption signals on chart paper. Measure the peak height of the standards and draw a calibration graph.

5. Calculation of the results

The absolute quantity (ng) of Au in the sample solution is read with the aid of a calibration graph established using 5, 10, and 20 ng standards. The net quantity is obtained by subtracting the average of three or more blank values for a run. The gold content in water is expressed as total soluble Au in ng per liter of water.

Quality Control:

The optimum working range is 5 ng - 50 ng Au/l.

The determination limit, expressed as three times the standard deviation of the reagent blank, is 3 ng/l.

The precision at 95% confidence limit (2σ), at the 10 ng/l level is ± 2 ng/l, based on 5 separate measurements carried out on spiked bulk control samples.

The accuracy is similar to the precision for this method.

Productivity:

A technician should be able to complete 18 determinations per week or about 4 determinations per day.

Additional Notes:

1. To avoid gold contamination, glassware, such as separatory funnels, must be cleaned thoroughly after being used. An effective procedure is as follows: Fill glassware with cleaning solution and allow to stand overnight. Wash with a stream of tap water and rinse with distilled water.
2. GFAAS absorbance signals vary from day to day. Calibration should be performed on a daily basis.
3. MIBK waste is not to be disposed of in the sink. It should be collected in a well labelled bottle, and the bottle should be tightly covered. A professional disposal firm will dispose of the bottle.
4. Avoid draining the MIBK layer through the stem of the separatory funnel. Instead, the MIBK portion should be picked up by a disposable pipette, and tranferred to a 10 X 75 mm test tube.

Bibliography:

Hall, G.E.M., Vaive, J.E., and Ballantyne, S.B., 1986, Field and Laboratory Procedures for Determining Gold in Natural Waters: Relative Merits of Preconcentrations with Activated Charcoal. Journal of Geochemical Exploration, Vol. 26, pp 191-202.

McHugh, J.B., 1984, Gold in Natural Water: A Method of Determination by Solvent Extraction and Electrothermal Atomization., Journal of Geochemical Exploration, Vol. 20, pp 303-310.

DETERMINATION OF FLUORIDE AUTOMATED COLORIMETRIC METHOD

Introduction:

The crustal abundance of fluorine is about 0.08%. Fluorine has an ionic radius just slightly smaller than oxygen and as a result can substitute for oxygen in oxy-minerals, if valency compensations are allowed. In some hydrous minerals such as amphiboles, mica and apatite, the replacement is quite easy. Fluorine also occurs in the following minerals: fluorite (CaF_2), topaz ($Al_2F_2SiO_4$), villiaumite (NaF) and amblygonite ($LiAlFPO_4$).

This automated procedure for the determination of fluoride in fused rock solution samples is based upon the distillation of hydrogen fluoride and subsequent reaction of the distillate with alizarin fluorine blue-lanthanum reagent to form a lilac-blue complex which is measured colorimetrically at 620 nm. The fusion and distillation processes are represented by the following chemical equations:

$$CaF_2 + 2\,NaOH \longleftrightarrow 2NaF + Ca(OH)_2$$

$$2\,NaF + H_2SO_4 \;\frac{\text{distillation}}{165^{\circ}C}\; 2HF + Na_2SO_4$$

Safety advisory:

1. This method makes use of various acids. Make sure that all pertinent MSDS sheets are reviewed before starting.

2. In preparation of the (1:1) H_2SO_4, slowly add sulphuric acid in portions to 500 ml of distilled water and mix well. Cool the solution in a water trough, and ensure that the temperature of the solution is kept below its boiling point during preparation.

3. Preparation of the acetate buffer solution and the alizarin fluorine blue stock solution should be carried out in a fume hood to avoid inhalation of vapors of glacial acetic acid and ammonium hydroxide.

Method:

This method consists of the following techniques:

1. Fusion and sample decomposition

2. Distillation for separation of analyte

3. Colorimetric measurement

4. Calculation of F concentration based on calibration curve produced from known standard solutions

Apparatus:

- Nickel crucibles, 40 ml
- Hot plate
- Plastic beakers, 50 ml graduated
- Lachat colorimeter with flow cell and 620 nm interference filter
- Recorder, Linear Model 1200
- Technicon Auto Analyzer II for fluoride analysis consisting of the following components:

    A. Sampler IV with 5 ml plastic sample cups
    B. Proportioning Pump III with pump tubes required for fluoride analysis. A flow diagram of the analytical system is shown in Figure F1.
    C. Microdistillation Apparatus (shown schematically in Figure F2) The major components include the following:

- Heating bath, equipped with electric heating bar, thermo-regulator and motor-driven stirrer
- 15 ft. Teflon coil, 1/8" i.d., immersed in the silicone oil contained in the heating bath
- rotary vacuum pump with vacuum gauge and regulator
- fractionation column of borosilicate glass
- water-jacketed condenser
- distillate collector
- waste condenser and trap assembly

    D. Cartridge consisting of housing which supports the reagents tubing, manifold, mixing coils, connectors and fittings.
    E. Voltage stabilizer.

Reagents:

- Sodium hydroxide pellets, NaOH, < 1 ppm fluoride
- Perchloric acid, $HClO_4$, (1:1)
- Sulphuric acid, H_2SO_4, (1:1)
- Acetone buffer, pH 4.0
- Acetone

- Alizarin fluorine blue
- Lanthanum nitrate stock solution
- Brij 35 wetting agent, 30% solution
- Alizarin reagent
- EDTA reagent, 1% w/v
- Stock standard flouride solution
- Working standard solutions

Procedures:

1. Reagent preparation

1.1. Perchloric acid, $HClO_4$, (1:1) - Mix 500 ml of perchloric acid (70%) with 500 ml distilled water.

1.2. Sulphuric acid, H_2SO_4, (1:1) - Carefully add 500 ml of concentrated sulphuric acid to 500 ml of distilled water. Mix and cool to room temperature before use.

1.3.1. Acetate buffer, pH 4.0 - Dissolve 60 g of sodium acetate trihydrate in 500 ml of distilled water.

1.3.2. Add 100 ml of glacial acetic acid and dilute to 1 liter with distilled water.

1.4.1. Alizarin fluorine blue (3-amino-ethylalizarin-N, N-diacetic acid) stock solution, 0.01M - Suspend 0.963 g of alizarin fluorine blue in about 100 ml of distilled water.

1.4.2. Add 2 ml of concentrated ammonium hydroxide and shake until the dye has completely dissolved.

1.4.3. Add 2 ml of glacial acetic acid and dilute to 250 ml with distilled water. Store in an amber bottle at 4°C.

1.5. Lanthanum nitrate stock solution, 0.01M - Dissolve 1.082 g of lanthanum nitrate, $La(NO_3)_3.6H_2O$ in 100 ml of distilled water and dilute to 250 ml with distilled water.

1.6.1. Alizarin reagent - Mix the solutions in the following order: 300 ml of acetate buffer, 150 ml of acetone, 50 ml of t-butyl alcohol, 36 ml of alizarin fluorine blue stock solution, 40 ml of lanthanum nitrate and 2 ml of Brij-35.

1.6.2. Dilute to 1 liter with distilled water. The reagent is stable for at least 2 days. Store at 4°C when not in use.

1.7. EDTA reagent, 1% w/v - Dissolve 10 g of tetrasodium ethylenediamine tetracetic acid, along with a few pellets of sodium hydroxide in distilled water and dilute to 1 liter.

2. Standard F solution preparation

2.1. Stock standard solution, 100 µg F/ml - Dissolve 0.2207 g of sodium fluoride in distilled water and dilute to 1 liter. Store in a polyethylene bottle.

2.2. Working standard solutions - Prepare 0.1, 0.2, 0.3, 0.5, and 1.0 µg F/ml standard solutions by serial dilution of the stock standard solution with distilled water. The standard solutions should contain 4 g of sodium hydoxide and 24 ml (1:1) perchloric acid per 100 ml in order to match the amounts of these substances used in alkali fusion of the rock samples. Store in polyethylene bottles.

2.3. Diluent - Dilute 25 ml of 100 µg F/ml stock standard solution to 1 liter with distilled water and mix.

3. Fusion and sample decomposition

3.1. Weigh out 0.050 g of rock sample and transfer into a 40 ml nickel crucible.

3.2. Add 0.2 g of sodium hydroxide pellets (approximately 12), and fuse the sample in a muffle furnace at 600°C for 5 minutes.

3.3. Remove the crucible and swirl to suspend all particulate matter.

3.4. Cool and dissolve the melt with water by heating the contents on a hot plate at low heat for half an hour.

3.5. Transfer the contents into a plastic beaker graduated at 50 ml.

3.6. Rinse the crucible with distilled water and add to the beaker. Add 12 ml (1:1) perchloric acid to dissolve the suspended particulates.

3.7. Dilute the sample to 50 ml with distilled water. Mix the solution thoroughly with a plastic stirring rod.

3.8. The solution is ready for the determination of fluoride by an AutoAnalyzer. One fusion blank is normally prepared for each 12 samples.

4. Measurement of F concentration

4.1. Start Up Procedure for AutoAnalyzer

4.1.1. Inspect tubing connections between distillation apparatus, sampler and proportioning pump and confirm that the analytical system is set up properly.

4.1.2. Turn on the heating bath. It takes about 1 hour to heat up the silicone oil to the preset temperature of 165°C.

4.1.3. Turn on colorimeter (warm-up time is 20 min.).

4.1.4. Fill the sample cups and place them in order on the sample tray. Mount the loaded sample tray onto the sampler.

4.1.5. Engage the pump platen and switch on the proportioning pump with all the reagent tubes dipped in distilled water.

4.1.6. Turn on the vacuum pump.

4.1.7. Gently turn on the cold water tap, and let the cold water flow steadily through the condensers and drain into the cup sink.

4.1.8. Switch on the recorder.

4.1.9. Check the vacuum system and the reagents flow system to ensure no leaks or spills. Distillate should now fill the collector.

4.1.10. Insert the reagent tubes into their corresponding solutions (Figure F1) and establish a baseline tracing on the recorder chart.

4.1.11. Press POWER push button to turn on the sampler.

4.1.12. The sample is pumped, together with (1:1) H_2SO_4 and air, through the teflon coil which is immersed in the heating bath. The fluoride in the sample reacts with sulphuric acid in the teflon coil to generate HF and water vapor which distill and condense into the collector, while the non-volatile solutions, including H_2SO_4 and $HClO_4$, are separated and drained off under vacuum. The distillate is pumped through the resample tube and combined with the alizarin fluorine blue reagent to develop a colored stream. The stream then passes through a flow cell and the absorbance is measured at 620 nm. Results appear as peaks traced on a chart recorder. The lag time from sampling to the appearance of a peak on the strip chart is about 3 minutes.

5. Calculation of the results

The fluoride concentration in the sample solution is read with the aid of a calibration curve, subtracting the blank value. The fluoride content of the rock sample is calculated in ppm according to the equation:

$$F = \frac{CV}{W}$$

where :

F = ppm of fluoride in rock

C = µg of F/ml of the sample solution

V = volume in ml of sample solution (usually 50 ml)

W = weight of sample in grams (usually 0.05 g)

6. Shutdown

6.1. Place all reagent tubes in distilled water and run water through the system for approximately 10 minutes.

6.2. Switch off the sampler when the sample probe is in the water reservoir position.

6.3. Switch off the recorder.

6.4. Switch off the colorimeter.

6.5. Switch off the proportioning pump and lift off the pump platen.

6.6. Turn off the vacuum pump.

6.7. Turn off the tap water.

6.8. Turn off the heating bath.

6.9. Lift off sample tray and discard sample solutions. Sample cup can be reused after rinsing with distilled water.

6.10. Discard the waste liquid in the liquid trap.

7. Maintenance

Cleaning of teflon distillation coil - This is accomplished by inserting the tygon tubes connected to the air inlet line of the distillation apparatus (Figure F2) briefly into 1 % Na_4EDTA solution. A quantity of the wash fluid will be swept through the teflon coil and will remove deposited material. When all particulate matter is removed from the coil, wash briefly with distilled water several times.

Pump tubes should be replaced after 200 working hours or prior to that if they become inflexible or flattened. They should always be left in a relaxed position when not in use.

The nickel crucible should be cleaned as soon as possible after use. The most effective way is to place them in hot 3N HCl for 10-15 min; transfer to a 5% NaOH solution and boil for half an hour; wash with Alconox solution; rinse with tap water and finally rinse with distilled water.

Quality control:

The optimum working range for the analytical system is 0.2 to 2.0 µg F/ml, which is equivalent to 200 - 2000 ppm in rock.

The determination limit is 40 ppm in rock.

The precision, expressed at the 95% confidence limit (2σ), is 10% (relative), e.g. 400 ppm ± 40 ppm.

The accuracy is comparable to the precision based on data collected from standard reference materials.

Productivity:

A technician should be able to complete 10 determinations per day.

Additional notes:

1. Do not allow the platen to remain down on the pump tubes when the pump in not operating. The fixed pressure will damage the pump tubes.
2. The vacuum gauge reading is set at 200-300 mm Hg. Adjustment is normally not required.
3. Occasionally, recovery of fluoride added to samples should be determined. Low values indicate a loss of fluoride possibly during pretreatment; high values indicate contamination.
4. The quality of alizarin fluorine blue is crucial to good performance. It has been necessary to check several suppliers to find an acceptable grade of reagent. Using good grade reagent, an intense colored complex formed with fluoride can be developed. The colour intensity or signal response can be monitored with a standard fluoride solution in order to determine whether the quality of the reagent is satisfactory.
5. Refer to Technicon operation manual for trouble shooting should instrumental problems arise.
6. Chloride and nitrate ions in percent concentrations can be distilled with fluoride ion and will interfere with the analysis by bleaching the alizarin fluorine blue - lanthanum reagent. Such high concentrations of chloride and nitrate are not expected in rock samples.
7. The alizarin working reagent is stable at 4°C for at least 7 days.
8. Samples with high fluoride concentration should be diluted to an appropriate level to fall within the optimum working range of 0.2 to 2.0 µg F/ml, with a solution containing 4g NaOH and 24 ml (1:1) $HClO_4$ per 100 ml.
9. By introducing diluent into the reacting stream as indicated in Figure F11, a linear calibration curve can be maintained, even at low concentrations of F.

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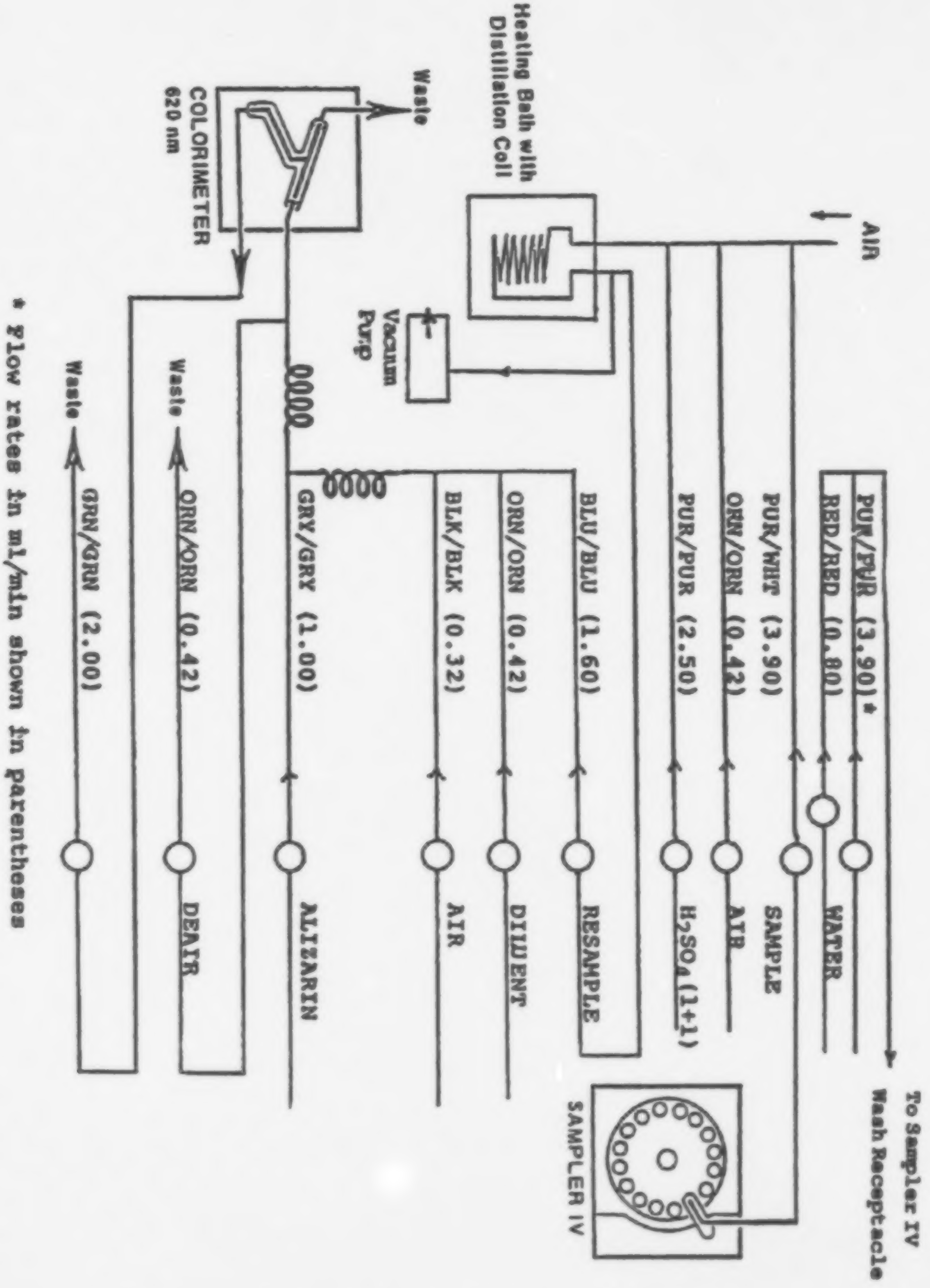
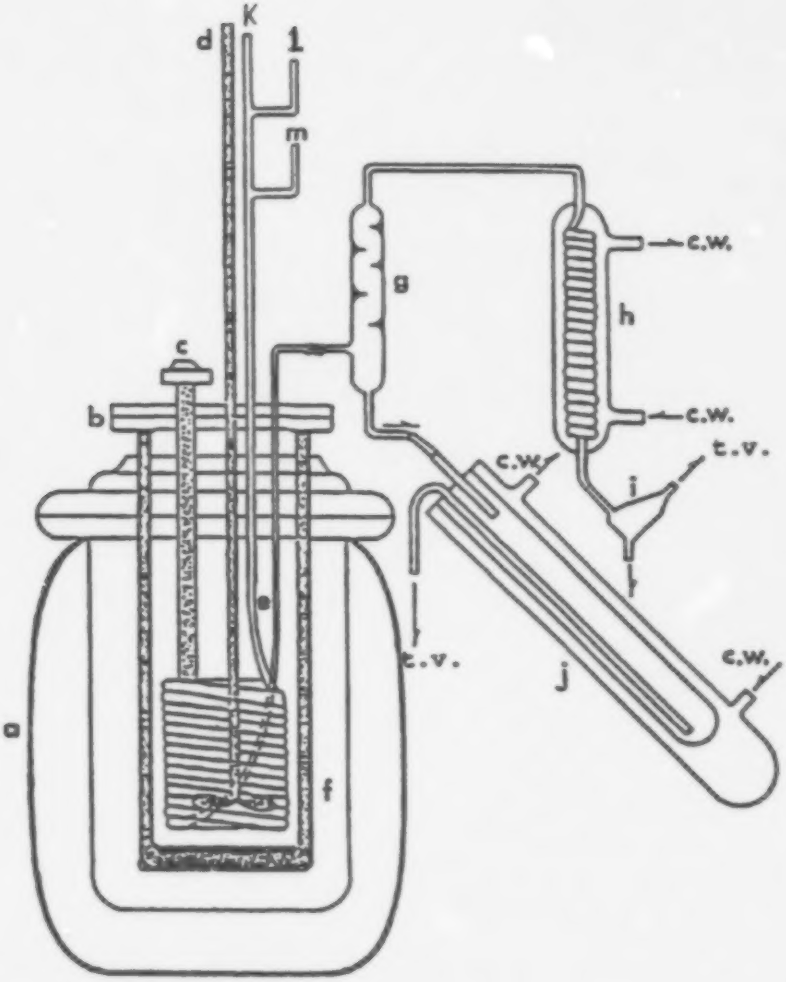

To Sampler IV
Wash Receptacle
AIR
Heating Bath with
Distillation Coil
Waste
COLORIMETER
620 nm
Vacuum
Pump
Waste
Waste
PUR/PUR (3.90)*
RED/RED (0.80)
PUR/WHT (3.90)
ORN/ORN (0.42)
PUR/PUR (2.50)
BLU/BLU (1.60)
ORN/ORN (0.42)
BLK/BLK (0.32)
GRY/GRY (1.00)
ORN/ORN (0.42)
GRN/GRN (2.00)
WATER
SAMPLE
AIR
H$_2$SO$_4$ (1+1)
RESAMPLE
DILUENT
AIR
ALIZARIN
DEAIR
SAMPLER IV
* Flow rates in ml/min shown in parentheses

Figure F1. Flow diagram of analytical system for fluoride (Range: 0-2 µg/ml).



(a)	Jacket of heating bath
(b)	Immersion electric heater
(c)	Thermometer - thermoregulator, range 0-200°C
(d)	Motor driven stirrer
(e)	Flexible Teflon tubing, 15ft long coiled on a rigid support
(f)	Silicone oil
(g)	Fractionation column of boro-silicate glass
(h)	Water-jacketed condenser
(i)	Distillate collector
(j)	Waste liquid condenser
(k)	Air inlet
(l)	Sample inlet
(m)	Sulfuric acid (1+1) inlet

c.w. refers to "cold water"

t.v. refers to "to vacuum"

Figure F2. Schematic drawing of microdistillation apparatus.

DETERMINATION OF CHLORIDE
AUTOMATED COLORIMETRIC FLOW INJECTION ANALYSIS METHOD

Introduction:

Chlorine is a strong hydrophile element and as a result concentrations of chlorine reported in rocks and minerals are erratic.

Chlorine has a larger ionic radius than oxygen and is not easily accommodated in the structure of most oxy-minerals. It has a similar ionic radius to sulphur, but does not readily substitute for sulphur in sulphide minerals.

Chlorine is precipitated in such minerals as apatite, mica, amphiboles, the sodalite family of minerals in nepheline syenite and related pegmatites, and in the scapolite family of minerals in granite pegmatites and contact metasomatic deposits.

Most chlorine removed from magmas by hydrothermal derivatives finds its way to the sea where it accumulates.

Chloride is determined by an automated colorimetric method using flow injection analysis (FIA) technique. The chemical principle of the method is that chloride reacts with mercuric thiocyanate to form mercuric chloride and liberate thiocyanate, which in turn reacts with the ferric ion to form a highly coloured complex that is stable and suitable for colorimetry. The absorbance of the coloured complex, which is proportional to the concentration of the chloride is measured at 480 nm. The chemical reactions involved are as follows:

$$Hg(SCN)_2 + 2Cl^- \longrightarrow HgCl_2 + 2(SCN)^-$$

$$3(SCN)^- + Fe^{3+} \longrightarrow \underset{\text{(coloured complex)}}{Fe(SCN)_3}$$

Safety advisory:

1. The following operations should be performed in a fume hood:

   A. Preparation of the 6% and 9% nitric acid solution.

   B. Preparation of ferric nitrate solution.

2. Lithium metaborate flux should be handled with care. Avoid inhalation and contact with the skin. In the process of mixing lithium metaborate with the sample, stir the contents gently to avoid the fine powder of flux being stirred up in the air.

Method:

The method consists of the following techniques:

1. Fusion and sample decomposition
2. Measurement of chloride signal using a Model 1000-300 Colorimeter, making use of the flow injection analysis technique
3. Calculation of chloride concentration based on a calibration curve produced from known standard solutions

Apparatus:

- A Lachat flow injection analysis system consisting of:

  A. Colorimeter (Model 1000-300)
  B. A single valve injection module (Model 1600-000)
  C. A sample/valve controller (Model 1000-150)

- Technicon Sampler II
- Technicon Proportioning Pump I with pump tubes required for chloride analysis. (A flow diagram of the analytical system is shown in Figure Cl1.)
- Strip chart recorder
- Graphite crucibles, 7.5 ml
- Teflon beakers, 50 ml
- Test tubes, calibrated at 15 ml

Reagents:

- Lithium metaborate, such as supplied by Spex Industries, Cat. No. L170
- Concentrated nitric acid, HNO_3, 12 N
- Nitric acid, HNO_3, 9%
- Nitric acid, HNO_3, 6%
- Ferric nitrate solution, $Fe(NO_3)_3.9H_2O$
- Mercuric thiocyanate solution, $Hg(SCN)_2$

- Stock standard solutions
- Working standard solutions

Procedures:

1. Reagent preparation

1.1. 9% Nitric acid - Dilute 90 ml of concentrated nitric acid and make up to 1 liter with distilled water.

1.2. 6% Nitric acid - Dilute 60 ml of concentrated nitric acid and make up to 1 liter with distilled water.

1.3. Ferric nitrate solution, 0.5 M. In a one liter volumetric flask, dissolve 202g of ferric nitrate in approximately 800 ml of distilled water. Add 25 ml of concentrated nitric acid and dilute to the mark. Mix thoroughly. Filter the solution if necessary.

1.4. Mercuric thiocyanate saturated solution - Dissolve 5 g of mercuric thiocyanate in 1 liter of distilled water and allow to stand for 4 hours.

2. Standard Cl solution preparation

2.1. Stock standard solution, 1000 μg Cl/ml - Dissolve 1.6485 g of sodium chloride, which has been dried in an oven at 105°C for several hours, in 1 liter of distilled water.

2.2. Working standard solution - Prepare 1, 2, 3, 4, and 5 μg Cl/ml standard solutions by serial dilution of the stock standard solution with 6% nitric acid.

3. Fusion and decomposition of sample

3.1. Weigh out 0.150 g of powdered rock sample and 0.300 g of anhydrous lithium metaborate into a graphite crucible. Mix thoroughly.

3.2. Fuse the sample at 860°C in a muffle furnace for 15 minutes.

3.3. Quickly transfer the molten sample into a 50 ml teflon beaker containing 10 ml of 9% nitric acid. Stir the solution using a magnetic stirrer for at least 1 hour to dissolve the fusion cake.

3.4. Transfer the contents to a test tube calibrated at 15 ml, and make to volume with distilled water. Seal the test tube with a piece of Parafilm, and mix the solution thoroughly.

3.5. Prepare a reagent blank simultaneously. Decant a portion of the solution to a sample cup for chloride determination as described below.

4. Measurement of Cl concentration

4.1. Turn on the power on all modules, except the sampler.

4.2. Place the reagent feedlines into the proper containers (see manifold in Figure Cl1).

4.3. Set the sampling time at 30 sec. and the washing time at 90 sec. on the sample/valve controller.

4.4. Place the calibration standards and sample solutions in the sample tray in order.

4.5. As soon as the system has stabilized and the baseline established, turn on the sampler. The standard and the sample solutions can then be run sequentially.

The mechanisms of flow injection analysis:

In performing flow injection analysis, samples and carrier are alternatively pumped into and flushed out of the sample loop which is mounted on the valve of the flow injection module. The sample loop is 56 cm long and 0.97 mm in diameter. Sampling time is 30 sec. and flushing time is 90 sec. The connection of these components and the analytical system are shown in Figure Cl1.

In position 1 (sampling) of Figure Cl1, the sample solution is picked up from the sample cup and is drawn by the action of the proportioning pump. It enters through port A of the injection valve filling the sample loop BC, and the excess exits through port D and drains out as waste. The sample flow path follows ABCD direction, while the flow path of the carrier, 6% HNO_3, is EF in order. The rotor of the injection valve then rotates 60 degrees and turns into position 2 (injection), changing the flow paths to AD and ECBF respectively. This permits the sample solution which has been collected in the loop BC to be propelled by the 6% HNO_3 carrier into the reacting stream. At the same time, the sample probe swings into the sampler reservoir in a synchronized motion with the rotor. The solution in the sample line, which is now 6% HNO_3, enters port A and exists through port D. This flow flushes out the tailings of the sample solution in preparation for a new cycle of sampling.

5. Calculation of the results

The chloride concentration, µg Cl/ml, in the sample solution is read with the aid of a calibration curve (blank being subtracted). Multiplying this value by a factor of 100, (15 ml/0.15 g), to obtain the chloride content in rock in ppm.

Quality Control:

The optimum working range for this method is 0.5 to 5.0 µg/ml in solution, equivalent to 50 to 500 ppm in rock.

The determination limit is 30 ppm.

The precision, expressed at the 95% confidence limit (2σ), is ± 10% relative, e.g. 250 ppm ± 25 ppm.

The accuracy is comparable to the precision, basec on data collected from standard reference materials.

Productivity:

A technician should be able to complete 15 determinations per day.

Additional notes:

1. In order to maintain a minimum blank value, a good grade of lithium metaborate (such as supplied by Spex Industries, Cat. No. L170) and nitric acid (such as the "Baker Analyzed" reagent) should be used.
2. If samples are low in chloride (less than 300 ppm), production rate can be increased by cutting down the washing time of the FIA system from 90 seconds to 60 seconds.
3. At the end of the analysis, place all feedlines in distilled water to flush system before turning off the power on all modules.

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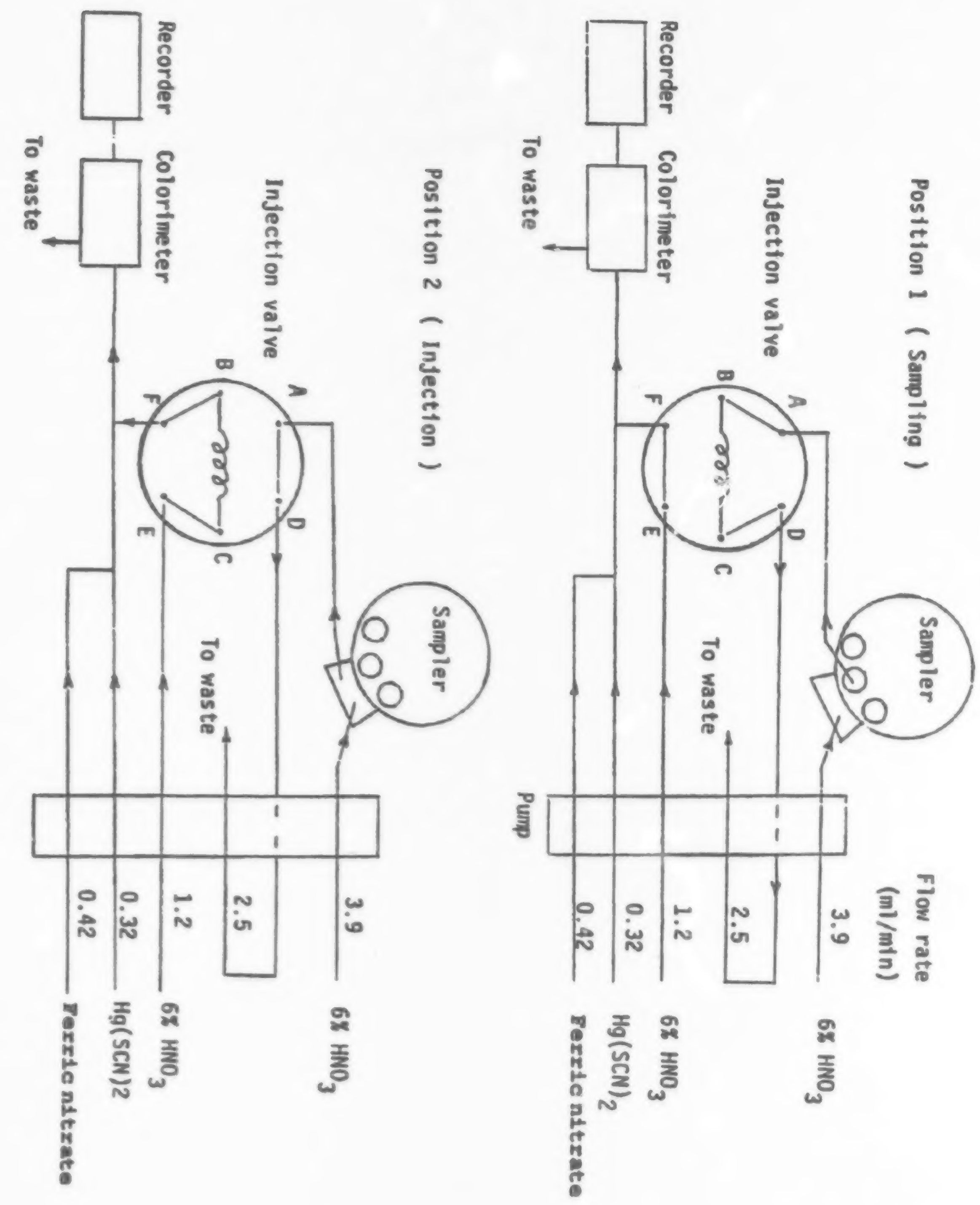
Position 1 (Sampling)
Flow rate (ml/min)
Sampler
Injection valve
A
B
C
D
E
F
Recorder
Colorimeter
To waste
To waste
Pump
3.9
2.5
1.2
0.32
0.42
6% HNO3
6% HNO3
Hg(SCN)2
Ferric nitrate
Position 2 (Injection)
Sampler
Injection valve
A
B
C
D
E
F
Recorder
Colorimeter
To waste
To waste
3.9
2.5
1.2
0.32
0.42
6% HNO3
6% HNO3
Hg(SCN)2
Ferric nitrate

Figure CL1. Analytical System and Reagent Manifold for the Determination of Chloride

THE DETERMINATION OF ARSENIC, ANTIMONY AND BISMUTH HYDRIDE GENERATION - ATOMIC ABSORPTION METHOD

Introduction:

Arsenic appears to follow sulphur quite closely, and as a result readily substitutes for sulphur in many sulphide minerals. Perhaps the best known arsenic bearing mineral is arsenopyrite. In ultrabasic rocks arsenic concentrations are typically 3 ppm while this decreases to about 1 ppm in intermediate rocks.

Antimony is less abundant in the earths crust than arsenic. It too is closely associated with sulphide minerals, but often shows higher concentrations in intermediate and acidic rocks.

Bismuth is generally less abundant than antimony. Bismuth occurs as a minor component of massive sulphide segregations, and in greater abundance in their derived hydrothermal deposits. It is also reported to be present in apatite of igneous rocks, and in many pematitic metamict minerals containing rare earth elements -possibly in the ferromagnesian minerals, or in plagioclase to some extent.

Arsenic, antimony and bismuth are individually determined by a hydride generation/atomic absorption method following sample decomposition.

This decomposition is accomplished in the following manner: for arsenic, the sample is fused with sodium hydroxide and brought into solution with hydrochloric acid; for antimony, the sample is digested with a mixture of sulphuric and hydrofluoric acids; and for bismuth, the sample is digested in a mixture of perchloric and hydrofluoric acids.

Sodium borohydride solution is introduced to the sample solution by means of an automatic sampler and a proportioning pump. The element of interest is converted to its hydride which is separated in a gas-liquid separator, then swept by a stream of argon into an electrically heated quartz tube atomizer. The atomic absorption of the element is measured.

Safety advisory:

1. When using HF wear glasses and gloves, and be extremely careful. More information on HF is available in the Geoscience Laboratories' Safety Manual page IV-17.
2. The sample tray and the waste bottles which collect the acidic drains from the hydride generator, should be covered to prevent the acid vapour from escaping to the ambient air. Good ventilation in the working area is essential.

Method:

The method consists of the following techniques:

1. Fusion and sample decomposition
    - A. Arsenic - fusion with sodium hydroxide and dissolution by hydrochloric acid
    - B. Antimony - decomposition by sulphuric and hydrofluoric acid
    - C. Bismuth - decomposition by perchloric and hydrofluoric acid

2. The elements are converted to hydride form by sodium borohydride

3. Measurement by atomic absorption spectrometry

4. Calculation of As, Sb and Bi concentrations based on a calibration curve produced from known standard solutions

Apparatus:

- Varian Model AA-6 atomic absorption spectrophotometer equipped with a model 9176, 1-100 MV recorder
- Technicon sampler II
- Technicon proportioning pump I
- Gas-liquid separator
- Gas impinger
- Quartz tube (16 cm long, 10 mm i.d. with an inlet tube fused into the centre), wound with a 22-gauge chromel A heating wire and insulated with a layer of wrapped Thermofab string
- Staco variable transformer
- Hot plate
- Nickel crucibles, 40 ml
- Stoppered graduated cylinder, 50 ml
- Glass beakers, 100 ml
- Teflon beakers, 30 ml
- Test tubes, borosilicate, 18 X 150 mm, graduated at 15 ml
- Test tubes, polystyrene, 16 X 150 mm

Reagents:

- Hydrochloric acid, HCl, 38%
- Borohydride solution
- Argon gas
- Sodium hydroxide pellets, NaOH
- Magnesium oxide
- Hydrofluoric acid, HF, 49.3%
- Sulphuric acid, H_2SO_4, 96%
- Potassium iodide solution
- Perchloric acid, $HClO_4$, 60%
- Digestion mixture
- Masking agent
- Stock arsenic standard solution (1000 µg/ml)
- Working arsenic standard solutions
- Stock antimony standard solution (1000 µg/ml)
- Working antimony standard solutions
- Stock Bismuth standard solution (1000 µg/ml)
- Working bismuth standard solutions

Procedures:

1. Reagent preparation

1.1.1. Borohydride solution - Dissolve 3 g of sodium borohydride in 300 ml of distilled water.

1.1.2. Add 3 pellets of sodium hydroxide. Store in a refrigerator when not in use.

1.2. Digestion mixture 1 - Mix equal volumes of hydrofluoric acid, sulphuric acid, and distilled water. Store in a polyethylene bottle.

1.3.1. Potassium iodide solution - Dissolve 10 g of potassium iodide in 100 ml of distilled water.

1.3.2. Add 2 pellets of sodium hydroxide.

1.4. Digestion mixture 2 - Mix hydrofluoric acid, perchloric acid and distilled water in the ratio of 2:2:1. Store in a polyethylene bottle.

1.5. Masking reagent - Dissolve 0.5 g each of thiosemicarbazide and 1,10-phenanthroline in 100 ml of 0.1M HCl solution.

2. Standard As, Sb, and Bi solution preparation

2.1.1. Stock arsenic standard solution (1000 µg/ml) - Dissolve 0.132 g of arsenic oxide (As_2O_3) in 2 ml of 1M NaOH, acidify with 1 ml of 10% (v/v) HCl, and dilute to 100 ml with distilled water.

2.1.2. Working arsenic standard solutions - Prepare 0.010, 0.020, 0.050 and 0.075 µg/ml standard solutions by serial dilution of the stock standard solution with 10% (v/v) HCl.

2.2.1. Stock antimony standard solution, 1000 µg/ml - Supplied by Harleco, specially prepared from $SbCl_3$ and standardized for use in atomic absorption.

2.2.2. Working standard solutions - Prepare 0.005, 0.010, 0.020, and 0.030 µg Sb/ml standard solutions by serial dilution of the stock standard solution with a mixture of 10% sulphuric acid and 20% hydrochloric acid.

2.3.1. Stock bismuth standard solution, 1000 µg/ml - Dissolve 1.1148 g of Bi_2O_3 in 20% (v/v) HCl, and dilute to 1 liter with the same acid.

2.3.2. Working standard solutions - Prepare 0.001, 0.002, 0.003, 0.005, and 0.010 µg Bi/ml standard solutions by serial dilution of the stock standard solution with 20% (v/v) HCl.

3. Fusion and sample decomposition

3.1.1. For As analysis - Weigh out 0.250 g of rock sample and transfer to a 40 ml nickel crucible. Add 0.1 g of magnesium oxide and 2 g (approximately 15 pellets) sodium hydroxide, and mix the dry contents of the crucible.

3.1.2. Fuse the sample in a muffle furnace at 550°C for 15 minutes.

3.1.3. Cool and leach the fusion cake with distilled water.

3.1.4. Transfer the solution with rinsing to a 100 ml glass beaker. Allow the contents to cool. Add 10 ml of concentrated HCl to the beaker.

3.1.5. Transfer the solution to a 50 ml graduated cylinder, and make to volume with distilled water. Stopper the cylinder and mix the solution thoroughly.

3.1.6. Prepare a reagent blank simultaneously.

3.2.1. For Sb analysis - Weigh out 0.100 g of rock sample and transfer to a 30 ml teflon beaker.

3.2.2. Digest the sample with 5 ml of acid digestion mixture 1 on a hot plate at low heat for approximately one hour (until white fumes of sulphuric acid appear and the volume is reduced to 1-2 ml). Avoid heating the contents to dryness.

3.2.3. Cool and dilute the contents with 10 ml of (1:4)HCl.

3.2.4. Heat the contents to near boiling and cool again to room temperature.

3.2.5. Reheat if any white precipitate is present.

3.2.6. Transfer the contents with rinsings to a borosilicate test tube graduated at 15 ml. Make to volume with (1:4)HCl. Seal the test tube with a piece of Parafilm and mix the solution thoroughly.

3.2.7. Prepare a reagent blank simultaneously.

3.3.1. For Bi analysis - Weigh out 0.100 g of rock sample and transfer to a 30 ml teflon beaker.

3.3.2. Digest the sample with 5 ml of the acid digestion mixture 2 on a hot plate at low heat for approximately one hour (until white fumes of perchloric acid appear and the volume is reduced to 1-2 ml).

3.3.3. Avoid heating the contents to dryness.

3.3.4. Cool and dilute the contents with about 5ml of (1:4)HCl.

3.3.5. Transfer the contents with (1:4)HCl, rinsing into a plastic test tube calibrated at 15 ml. Make to volume with (1:4)HCl. Mix the solution thoroughly and allow the residue to settle.

3.3.6. Prepare a reagent blank simultaneously.

4. Measurement of As, Sb, and Bi concentrations

4.1. Setting up the hydride generator - Set up the hydride generation equipment as depicted in Figure As1., using appropriate tube manifold. Mount the quartz tube on a burner head, with its inlet connected to a tygon tubing leading to the hydride generator.

4.2. Turn on the power of the Varian AA-6 atomic absorption spectrophotometer. Select the instrumental parameters according to the order given in the following table:

	As	Sb	Bi
Wavelength, nm	193.7	217.6	223.2
Lamp Current, mA	7	10	8
Slit Width, µ	300	100	50
Damping	B	C	C
Expansion	5	5	6
Recorder span, mV	20	10	10
Recorder chart speed, cm/min	0.5	1.0	1.0
Variable transformer dial	40	40	40
Flowmeter reading	4	4	4
Sample time/wash time	40s/60s	45s/45s	45s/45s

4.3. Load the sample solutions which are prepared on a batch basis, in the sample cups and place them in order into the slots of a sample tray held on an automatic sampler. After the hollow cathode lamp has warmed up, align the quartz tube with the light beam to allow maximum radiation to reach the detector.

4.4. Obtain the required temperature (850°C ± 20°C) of the quartz tube atomizer by switching on the pre-set variable transformer. Turn on the proportioning pump with all the reagent tubes dipped in the water. Introduce argon immediately with its flow rate regulated by a flowmeter. As soon as the system has stabilized, insert the reagent tubes into their corresponding solutions. Establish a baseline signal. Switch on the automatic sampler. The standard, sample and blank solutions will then be analysed continuously. Record the absorption signals on chart paper. Measure the peak heights of the standards and draw a calibration graph.

5. Calculation of the results

The concentration of the element in the sample solution is read from the calibration graph. Subtract the blank to obtain the net concentration. Calculate the content of the element in rock according to the corresponding formula as shown in the following table:

As

Sample wt/vol	0.25g/50ml
µg/g (ppm) in rock	µg/ml x 200ml/g

Sb

Sample wt/vol	0.10g/15ml
µg/g (ppm) in rock	µg/ml x 150ml/g

Bi

Sample wt/vol	0.10g/15ml
μg/g (ppm) in rock	μg/ml x 150ml/g

Quality Control:

Optimum working range is 0.01-0.05 μg/ml for As, 0.005-0.030 μg/ml for Sb and 0.002-0.010 μg/ml for Bi (where no excessive interferences were noted).

The determination limits (expressed as concentrations in rock samples) for the three elements are 1.0 ppm for As, 0.1 ppm for Sb, and 0.05 ppm for Bi.

The precision for each element, expressed at the 95% confidence limit (2σ), is ± 10% for As, ± 14% for Sb, and ± 12% for Bi (relative).

The accuracy for each element is comparable to their respective precisions based on data collected from standard reference materials.

Productivity:

A technician should be able to complete 20 samples per day for each element.

Additional Notes:

A. General comments about all three elements:

1. The effect of argon flow rate on absorption signal is significant, and the flow rate should not be changed or readjusted in the midst of an analysis.

2. Accumulation of deposit of heavy metals in the glass fittings may occur after running a large number of samples. The fittings can be easily cleaned by pumping 1% (v/v) hydrogen peroxide and 5% EDTA solutions in sequence.

3. The impinger filled with concentrated sulphuric acid acts as a gas mixer and moisture absorber. It has the effect of homogenizing the gas mixture and hence reducing the signal noise.

4. It should be noted that mutual interference effects between the hydride-forming elements exist. If the concentration ratio of the other hydride-forming element or elements to the analyte is higher than 100, standard addition technique should be employed to ensure correct results. The tolerance limits of the hydride-forming elements can also be served as a guide line for determining the problem. These tolerance limits can be found in the literature such as some of those quoted in the bibliography.

B. Comments specific to As determination:

5. Magnesium oxide is used in the fusion of sample to capture any arsenic which may otherwise escape due to volatilization.

6. The fusion cake in the nickel crucible can be dissolved in distilled water more readily if it is warmed on a hot plate at low heat for half an hour.

7. Cu and Ni in concentrations of 20 and 10 μg/ml interfere with the analysis.

8. For samples containing organic materials, addition of approximately 1 ml or more of concentrated nitric acid during digestion is recommended.

C. Comments specific to Sb determination:

9. Avoid digesting the sample to dryness which will result in loss of Sb.

10. Potassium iodide is an essential component of the analysis system. It quantitatively pre-reduces Sb^{+5} in the presence of HCl to Sb^{+3} prior to the reaction with sodium borohydride, and hence improves the sensitivity as well as the precision of the determination.

11. When the system is ready to run, it is good practice to condition it first by repeatedly analyzing a standard solution until a constant signal is attained prior to the actual analysis.

12. Cu, Ni, and As in high concentrations interfere with Sb analysis. The tolerance limits are 3000, 1500 and 750 ppm in rock respectively

13. For samples containing organic materials, addition of approximately 1 ml of concentrated nitric acid during digestion is recommended.

D. Comments specific to Bi determination:

14. Avoid digesting the sample to dryness which will result in loss of Bi.

15. A batch of 40 samples can be digested simultaneously on a hot plate with ease.

16. The digested solution should be kept in plastic test tubes.

17. Thiosemicarbazide and 1,10-phenanthroline are used as masking agents for Bi to minimize interferences from Cu and Ni.

18. When the system is ready to run, it is a good practice to condition it first by repeatedly analyzing a standard solution until a constant signal is attained prior to the actual analysis.

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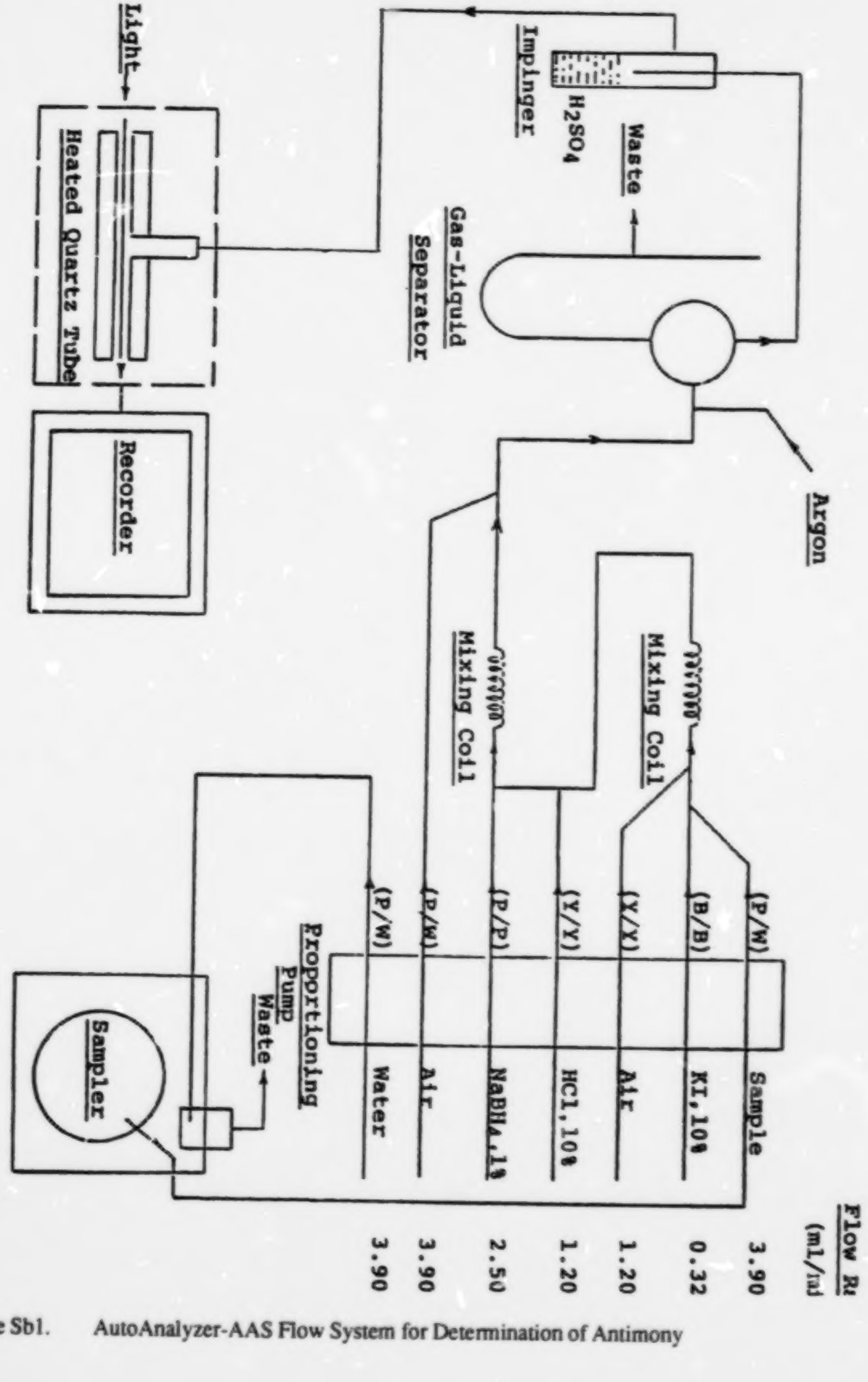
Light
Heated Quartz Tube
Recorder
Impinger
H_2SO_4
Waste
Gas-Liquid Separator
Argon
Mixing Coil
Mixing Coil
Proportioning Pump
Waste
Sampler
Flow R
(ml/m
(P/W) Sample 3.90
(B/B) KI,10% 0.32
(Y/Y) Air 1.20
(Y/Y) HCl,10% 1.20
(P/P) $NaBH_4$,1% 2.50
(P/W) Air 3.90
(P/W) Water 3.90

Figure Sb1. AutoAnalyzer-AAS Flow System for Determination of Antimony

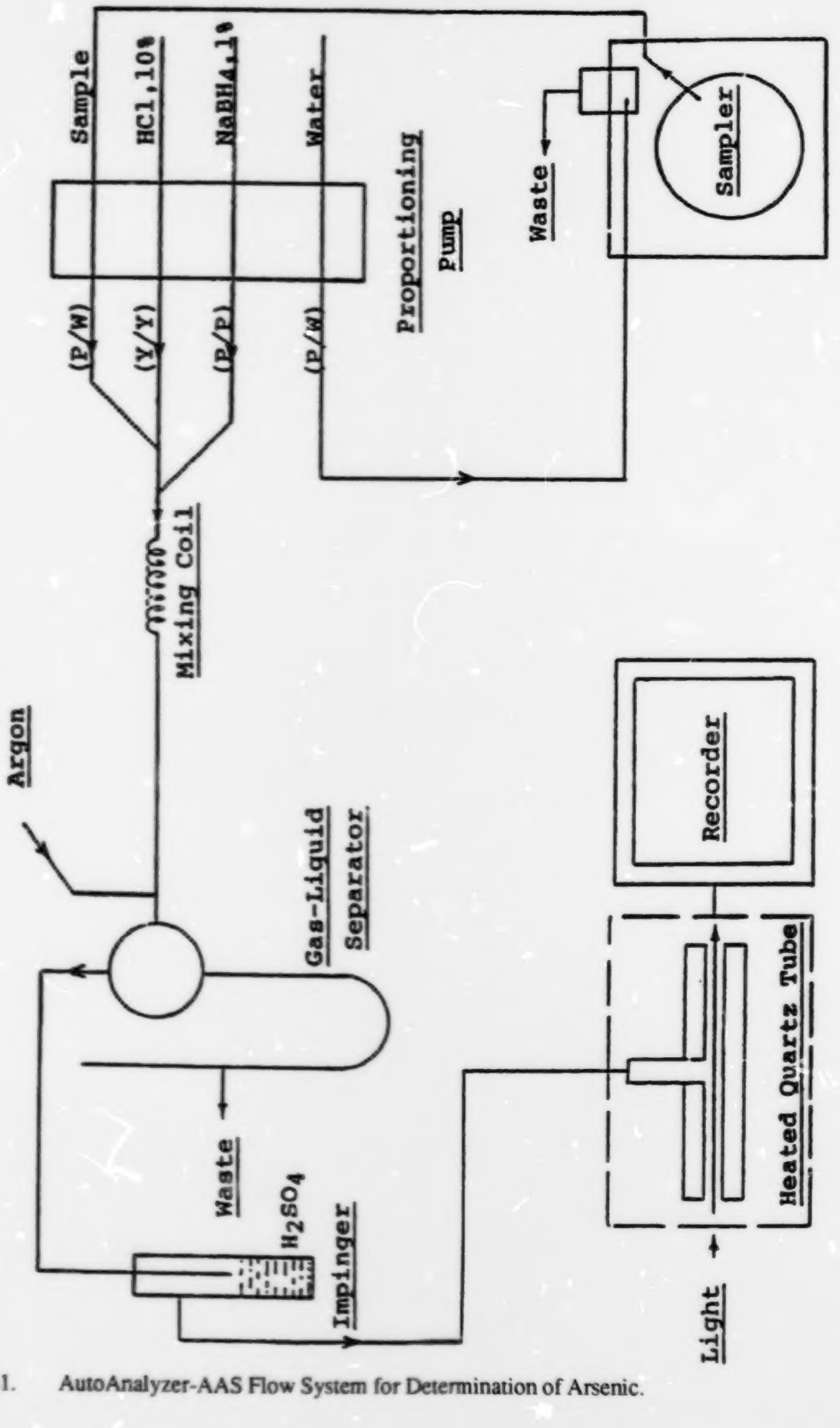
Sample
HCl, 10%
NaBH4, 1%
Water
(P/W)
(Y/Y)
(P/P)
(P/W)
Proportioning Pump
Waste
Sampler
Mixing Coil
Argon
Gas-Liquid Separator
Waste
H2SO4
Impinger
Recorder
Heated Quartz Tube
Light

Figure As1. AutoAnalyzer-AAS Flow System for Determination of Arsenic.

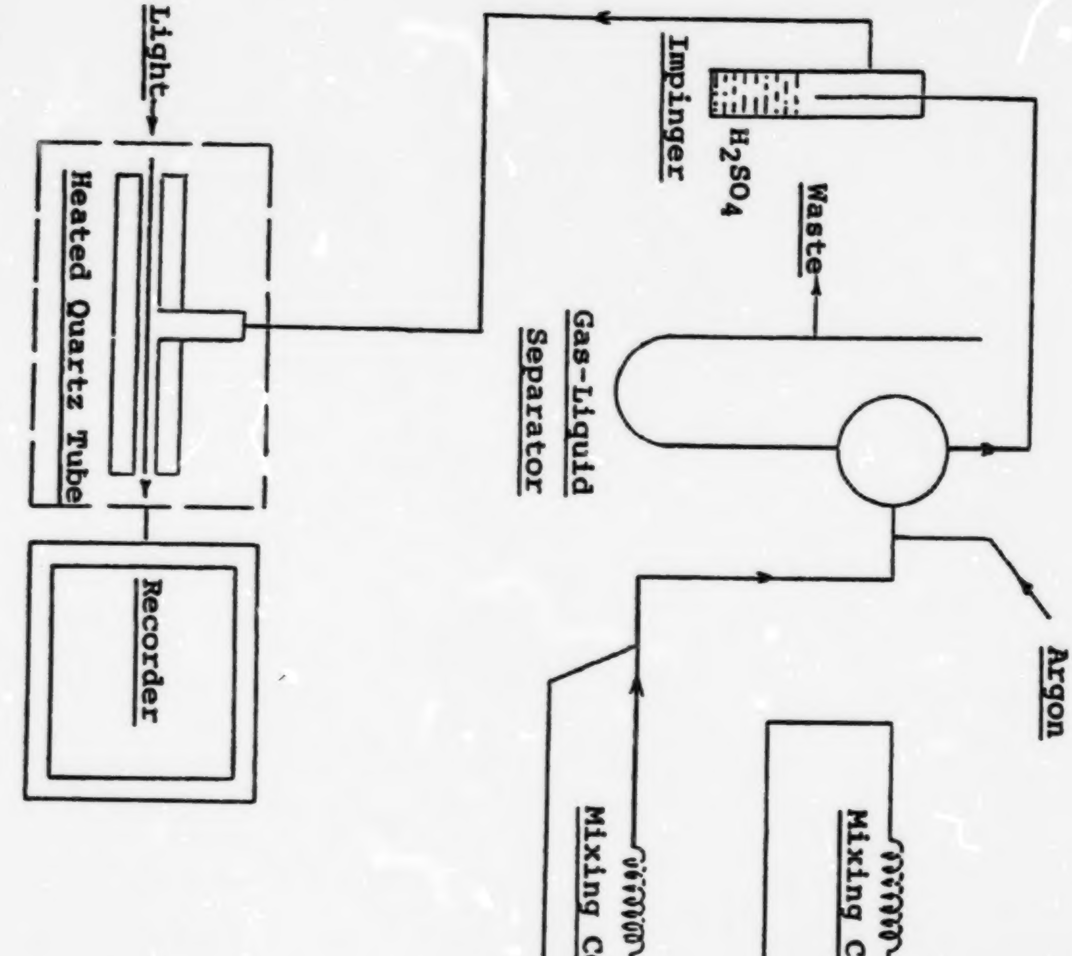
Light
Impinger
H_2SO_4
Waste
Gas-Liquid Separator
Heated Quartz Tube
Recorder
Argon
Mixing Coil
Mixing Coil
(P/W) Sample
(B/B) Masking Reagent
(Y/Y) Air
(Y/Y) HCl,10%
(P/P) NaBH4,1%
(P/W) Air
(P/W) Water
Proportioning Pump
Waste
Sampler

Figure Bi1. AutoAnalyzer-AAS Flow System for Determination of Bismuth.

DETERMINATION OF SELENIUM
HYDRIDE AAS - AUTOMATED FLOW INJECTION ANALYSIS

Introduction:

In igneous rocks, selenium follows sulphur very closely. Therefore, selenium is usually present in detectable amounts in all sulphide minerals in massive segregations, contact metasomatic deposits, veins, pegmatites and in desseminated accessory form in igneous rocks. Selenium substitutes for sulphur in these environments and occasionally forms separate selenides of Cu, Pb, Ag etc.

In high temperature deposits, selenium concentrations can be in the range of 15 to 60 ppm, while in medium to low temperature deposits, it may occur in the 1 to 5 ppm level.

The rock sample is digested with a mixture of hydrofluoric, nitric and perchloric acids. The acidified sample solution is introduced into a carrier stream by a flow injection module in conjunction with an autosampler and a proportioning pump. The carrier stream is merged with sodium borohydride solution to bring about a redox reaction between the reductant and the selenium in the sample.

Selenium is converted to its hydride which is separated in a gas-liquid separator and swept by a stream of argon into an electrically heated quartz tube atomizer. The atomic absorption of selenium is measured at 196.0 nm.

The concentration of selenium in the sample solution is read from a calibration graph, and the content of selenium in rock is calculated according to the sample weight and total volume of the sample solution.

Safety advisory:

1. When using HF wear glasses and gloves, and be extremely careful. More information on HF is available in the Geoscience Laboratories' Safety Manual page IV-17.

2. The sample tray and the waste bottles which collect the acidic drains should be covered to prevent the acid vapour from escaping to the ambient air. To ensure a clean air working environment, good ventilation is recommended.

Method:

The method consists of the following techniques:

1. Sample decomposition

2. Separation and concentration by hydride reduction

3. Measurement of selenium signal using Atomic Absorption Spectrometry

4. Calculation of selenium concentration based on a calibraton curve produced from known standard solutions

Apparatus:

- Varian Model AA-6 atomic absorption spectrometer equipped with a model 9176 strip-chart recorder.
- Technicon Sampler II
- Technicon Proportioning Pump I
- Flow injection module (Model No. 1000-600, Lachat Instruments)
- Gas-liquid separator
- Gas impinger
- Quartz tube (16 cm long, 10 mm i.d. with an inlet tube fused into the centre), wound with a 22-gauge Chromel A heating wire and insulated with a layer of wrapped Thermofab string
- Staco variable transformer
- Teflon beakers, 30 ml
- Hot plate
- 18 x 150 mm test tubes, graduated at 15 ml

Reagents:

- Hydrofluoric acid, HF, 48%
- Perchloric acid, $HClO_4$, 60%
- Hydrochloric acid, HCl, 38%
- Nitric acid, HNO_3, 70%
- Digestion mixture
- Reducing solution
- Masking agent
- Stock selenium standard solutions, 1000 μg/ml

Procedures:

1. Reagent preparation

1.1. Digestion mixture - Mix hydrofluoric acid, perchloric acid, nitric acid, and distilled water in the ratio of 4:4:1:1 respectively and store in a polyethylene bottle.

1.2. Reducing solution - Dissolve 5 g of sodium borohydride and five pellets of sodium hydroxide in 500 ml of distilled water. Store in a refrigerator when not in use. The solution is stable at 4°C for at least a week.

1.3. Masking reagent - Dissolve 1 g of 1,10-phenanthroline in 100 ml of 0.1M HCl.

2. Standard Se solution preparation

2.1. Stock Se Standard Solution, 1000 µg/ml - Dissolve 0.100 g of powdered selenium in 100 ml of 10% nitric acid.

2.2. Working standard solutions - Prepare 0.25, 0.50, 1.0, 2.0 and 4.0 ng/ml solutions by serial dilution of the stock standard solution with 3.6N HCl.

3. Sample decomposition

3.1. Digest 0.200 g of rock sample with 5 ml of digestion mixture in a 30 ml teflon beaker on a hot plate for about one hour or until white fumes of perchloric acid appear and the volume of the contents reduces to approximately 1 ml.

3.2. Cool and add about 2 ml of distilled water, and 4.5 ml of concentrated HCl.

3.3. Heat the contents to just under boiling for several minutes to reduce Se that is in Se^{6+} oxidation state to Se^{4+}.

3.4. Cool and transfer the contents to a test tube calibrated at 15 ml.

3.5. Make to volume with distilled water.

3.6. Seal the test tube with a piece of Parafilm and mix the solution thoroughly. The concentration of HCl in the sample solution is now 3.6N (30% v/v).

3.7. Prepare a reagent blank simultaneously.

3.8. Decant a portion of the solution to a sample cup for subsequent AAS determination.

4. Measurement of Se concentration

Instrument parameters

Atomic absorption spectrometer		
	Wavelength	196.0 nm
	Lamp current	8 mA
	Slit width	300 µ
	Damping	C (Maximum)
	Expansion	6
Flow injection module		
	Sample time	30 sec
	Washing time	40 sec
Variable transformer		
	Dial	50
	(set to produce 850 +/- 20°C in the atomizer)	
Recorder		
	Span	10 mV
	Chart speed	1 cm/min.
Argon		
	Flow rate	300 ml/min.

Set up the hydride generation equipment and connect the tubing that leads to and from the injection valve of the flow injection module according to the layout shown in Figure Se1. Mount the quartz tube on the burner with its side arm connected to the hydride generator with tygon tubing. Align the quartz tube with the light beam to allow maximum radiation to reach the detector. Switch on the preset variable transformer to provide the desired temperature in the atomizer. Turn on the proportioning pump with all the reagent tubes dipped in water. Introduce the argon immediately with its flow rate regulated at 300 ml/min.

Turn on the flow injection module which is interfaced with the sampler. The motions of the injection valve and the sample probe are synchronized. Set the sampling time to 30 sec. and the washing time for 40 sec. on the flow injection module. Insert the reagent tubes into the corresponding solutions (see arrangement in Figure Se1). As soon as the system has stabilized and the baseline is established, the standard and sample solutions which have been loaded in the sampler can then be run sequentially.

In position 1 of Figure Se1, the sample solution is picked up from the sample cup and is drawn through the sample tubes (line 4a and 4 in Figure Se1) by the action of the peristaltic pump. It enters port A of the injection valve, filling up the sample loop AB, and the excess exits through port B. The rotor of the injection valve then rotates a quarter turn so that ports A and B interchange places with ports C and D (position 2, Figure Se1), permitting the sample solution in the loop AB to be propelled by the 5% HCl carrier into the reacting stream. At the same time, the sample probe swings into the sample reservoir in a synchronized motion with the rotor. The solution in sample line (4a), which is now 5% HCl, enters port C and exits through port D. This flow will flush out the tailings of the sample solution, in preparation for a new cycle of sampling.

5. Calculation of the results

When the analysis is complete, calculate the Se concentration from a calibration plot of peak height vs. concentration which is linear up to 4 ng Se/ml.

Read the concentration of Se in the sample solution from the calibration graph. Subtract the blank value to obtain the net concentration (ng Se/ml). Calculate the selenium content in the rock sample according to the formula:

$$ng\ Se\ /g\ in\ rock = ng\ Se\ /ml\ x\ \frac{15\ ml}{0.2\ g}$$

$$= ng\ Se\ /ml\ x\ 75\ ml\ /g$$

Quality control:

The optimum concentration range for selenium is 50 to 300 ng/g.

The determination limit of this method is 20 ppb in rock samples.

Precision, expressed at the 95% confidence limit (2σ), is 12% (relative).

Accuracy is comparable to the precision based on data collected from standard reference materials.

Productivity:

A technician should be able to complete 20 determinations per day.

Additional Notes:

1. Avoid digesting the sample to dryness which will result in loss of Se.
2. Nitric acid is an essential ingredient for sample digestion.
3. Because of the absorbance of Se^{4+} is much stronger than that of Se^{6+}; Se in the digested sample solution, mainly in the form of Se^{6+}, must be reduced to Se^{4+} by hot HCl (8-12M) prior to determination.
4. 1,10 phenanthroline is used as a masking agent to minimize interferences from Cu and Ni.
5. Cu and Ni in high concentrations will interfere with the analysis. The tolerance limits are 0.3 and 4.0% in rock respectively.

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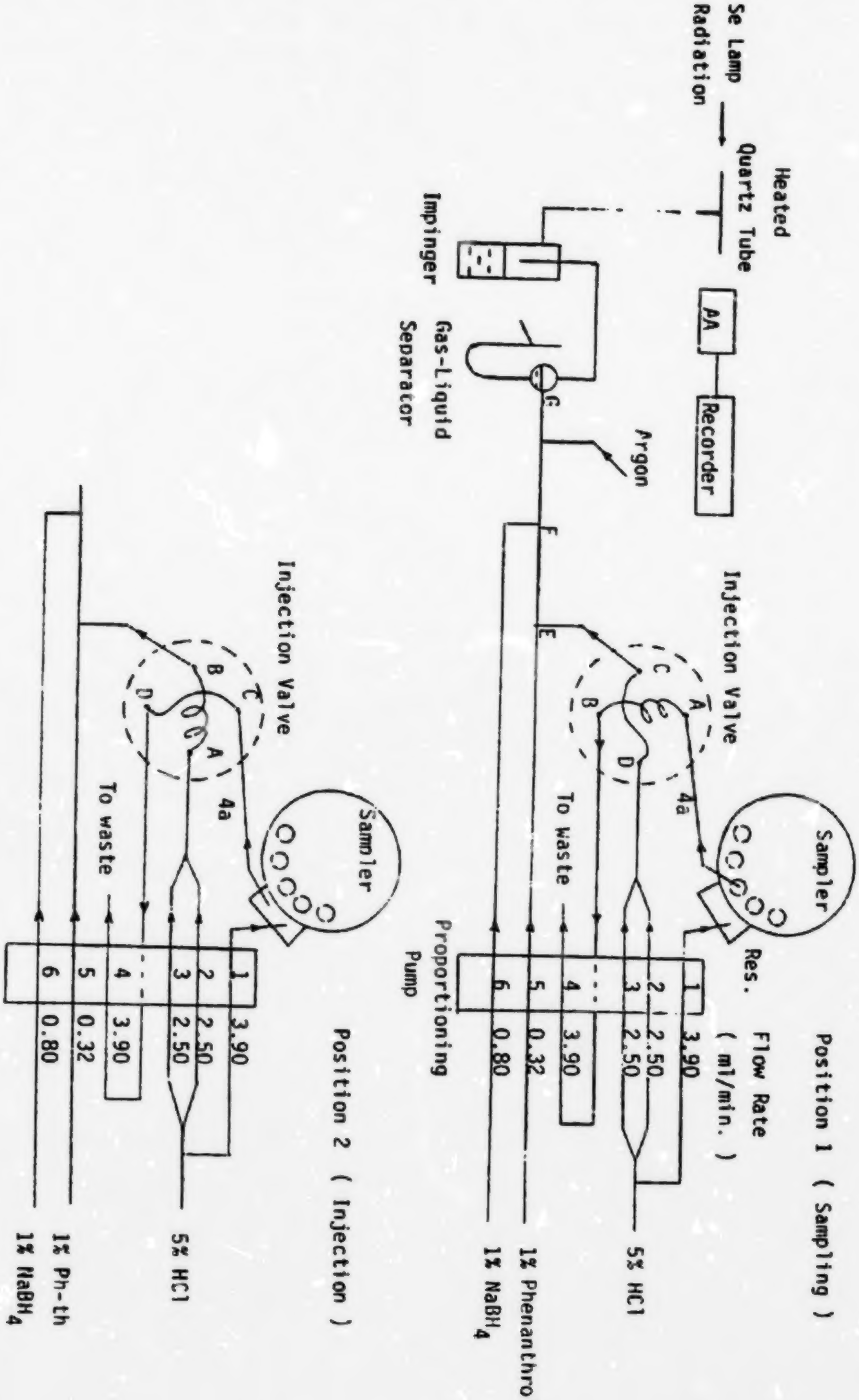
Se Lamp Radiation
Heated Quartz Tube
AA
Recorder
Impinger
Gas-Liquid Separator
G
Argon
F
E
Position 1 (Sampling)
Injection Valve
A
B
C
D
4a
Sampler
To waste
Res.
Proportioning Pump
Flow Rate (ml/min.)
1
2
3
4
5
6
3.90
2.50
2.50
3.90
0.32
0.80
5% HCl
1% Phenanthroline
1% NaBH$_4$
Position 2 (Injection)
Injection Valve
A
B
C
D
4a
Sampler
To waste
1
2
3
4
5
6
3.90
2.50
2.50
3.90
0.32
0.80
5% HCl
1% Ph-th
1% NaBH$_4$

Figure Se1. Analytical Manifold for the Determination of Se by Automated Flow Injection and Hydride - AA Techniques.

DETERMINATION OF MERCURY
COLD VAPOR FLAMELESS ATOMIC ABSORPTION METHOD

Introduction:

A major challenge in Hg analysis lies in the preparation and storage of geological samples prior to analysis. This is due to the high vapor pressure of mercury, its presence in the atmosphere, and the generally low levels in naturally occurring materials. A number of procedures developed to allow for the above factors are detailed below.

Soil samples are normally collected at a depth of 4 to 6 inches. As the Hg concentration in soils often varies considerably within a soil profile, a standardized depth of collection is important. In areas with a thick organic horizon, such as British Columbia, samples should be collected below the obvious organic horizon.

If the soil samples are dry they should be sieved to -80 mesh in the field, using a stainless steel sieve, and stored in air-tight screw top glass vials.

Wet samples should be dried at room temperature or in the shade before sieving. Heat lamps should not be used as this could result in volatilization of Hg from the sample.

Rock samples should not be ground in a ceramic plate mill. The heat generated by such grinding tends to volatilize a significant portion of the included Hg, especially in samples containing sulphides.

Instead, rock samples should be coarsely crushed in a jaw crusher and the +20 mesh fraction removed. This fraction should then be hand ground to -80 mesh. Sample pulps should then be stored in air-tight glass vials.

The sample is digested at low heat with nitric and hydrochloric acids. The digested sample and stannous chloride solution are continuously pumped through a mixing coil and into a gas-liquid separator. Mercuric ions present in the solution are reduced to elemental mercury. The volatilized mercury is separated and swept by a stream of argon into the absorption cell of a LDC/Milton Roy Mercury Monitor where the atomic absorption at 253.7 nm is measured.

Safety advisory:

1. Ultraviolet radiation is emitted from the mercury lamp when the instrument is on. Do not remove the lamp cover while the instrument is on without suitable eye protection.

Installation of a mercury scrubber at the vent of the cell chamber of the mercury monitor is recommended. The scrubber is made of a small tube loosely packed with dry moss (sphagnum) and a few gold chips. It will serve as a mercury trap, preventing the hazardous vapor from escaping to the ambient air.

Method:

The method consists of the following techniques:

1. Sample decomposition

2. Measurement of mercury absorption signal by a LDC/Milton Roy Mercury monitor

3. Calculation of mercury concentration based on a calibration curve produced from known standard solutions

Apparatus:

- LDC/Milton Roy Mercury Monitor
- Technicon Sampler II
- Technicon Proportioning Pump I
- Gas-liquid separator
- Drying tube filled with magnesium perchlorate
- Flowmeter
- Test tubes, Pyrex No. 7900, graduated at 25 and 50 ml
- Hot plate
- Thermometer
- Aluminum heating block, 2" x 4" x 6" with 12 wells to hold test tubes and one small well to hold thermometer
- Vortex-Genie mixer
- Linear strip-chart recorder

Reagents:

- The following reagents should be free of mercury and reagent grade:
- Hydrochloric acid, HCl, 38%, such as Ultrex Ultrapure grade supplied by Baker Chemical Company
- Nitric acid, HNO_3, 70%
- Potassium dichromate solution (2% w/v)
- Stannous Chloride solution (30% w/v)

- Hydroxylamine hydrochloride solution (5% w/v)
- Mercury standard stock solution (1000 μg/ml Hg), such as supplied by Baker Chemical Co.
- Mercury standard solutions
- Mercury working standard solutions

Procedures:

1. Reagent preparation

1.1. 10% Nitric acid (v/v) - Prepare 2 liters of solution by diluting 200 ml of concentrated nitric acid with 1.8 liters of distilled water.

1.2. 20% Nitric acid (v/v) for sample dilution purposes - Prepare 2 liters of solution by diluting 400 ml of concentrated nitric acid with 1.6 liters of distilled water.

1.3. Potassium dichromate solution (2% w/v) - Dissolve 4 g of $K_2Cr_2O_7$ in 200 ml of distilled water.

1.4. Stannous chloride solution (30% w/v) - Dissolve 60 g of stannous chloride in 60 ml of concentrated HCl, and dilute to 200 ml with distilled water.

1.5. Hydroxylamine hydrochloride solution (5% w/v) - Dissolve 10 g of hydroxylamine hydrochloride in distilled water and make up to 200 ml.

2. Standard Hg solution preparation

2.1. Mercury standard solutions

2.1.1. 1 μg/ml Hg solution - Prepare by serial dilution of the 1000 μg/ml Hg stock solution with 20% nitric acid.

2.1.2. 25 ng/ml Hg solution - Prepare by serial dilution of the 1 μg/ml Hg stock solution with 20% nitric acid.

2.1.3. Store solutions in a glass container.

2.2. Mercury working standard solutions

2.2.1. 0.5 and 1.0 ng/ml Hg standard solutions are prepared by serial dilution of the 25 ng/ml Hg solution with 20% nitric acid. These solutions are stable for at least two months.

2.2.2. Store solutions in a glass container.

3. Sample decomposition

3.1. Weigh out 0.250 g of sample and transfer into a Pyrex No. 7900 test tube.

3.2. Add 5 ml of concentrated nitric acid and 0.5 ml of concentrated hydrochloric acid to the sample. Mix the contents. Place the test tube in a well in the aluminum block.

3.3. When a batch of samples, including the blank, have been prepared in the same way, place the aluminum block on the hot plate and maintain a temperature of 110°C.

3.4. Insert a thermometer in the small well in the aluminum block to monitor the temperature.

3.5. Digest the sample for two hours.

3.6. Add the 2% $K_2Cr_2O_7$ solution dropwise to the sample with shaking until the orange color persists.

3.7. Place the test tube into a test tube rack (or into another aluminum block) and let cool at room temperature.

3.8. Add distilled water to the test tube and make to the 25 ml mark. Mix the solution thoroughly using a vortex mixer.

3.9. Allow the residues to settle (about one hour). Transfer the supernatent sample solution to a sample cup for Hg determination.

4. Measurement of Hg concentration

4.1. Turn on the power switch of the LDC/Milton Roy Mercury Monitor, and check that the energy meter settles in the 0.2 to 0.5 milliamperes range.

4.2. Select the optimum absorbance range (normally at 0.08 position).

4.3. Turn on the recorder. Set the span at 1 mV and chart speed at 1 cm/min.

4.4. Set up the auto analyzer system using the tube manifold as depicted in Figure Hg1.

4.5. Load the sample cups containing the sample solutions, including the standard and blank solutions, into the slots of a sample tray held on the automatic sampler.

4.6. Turn on the proportioning pump with all the reagent tubes dipped in distilled water.

4.7. Turn on the argon cylinder and introduce argon to the reacting stream with the argon flow-rate regulated by the flowmeter at dial setting 30.

4.8. Once the system has stabilized, insert the reagent tubes into their corresponding solutions.

4.9. Re-stabilize the system and establish a baseline on the recorder chart.

4.10. Switch on the automatic sampler. The standard, sample, and blank solutions will then be run sequentially.

4.11. Record the absorption signals on a recorder chart.

4.12. Measure the peak heights and draw a calibration graph.

Read the concentration of Hg in the sample solution from the calibration graph. Subtract the blank value to obtain the net concentration (ng Hg/ml). Calculate the Hg concentration in the rock sample according to the formula:

$$\begin{aligned} ng\ Hg/g\ \ in\ rock &= ng\ Hg/ml\ \ x\ \frac{25\ ml}{0.25\ g} \\ &= ng\ Hg/ml\ \ x\ 100 ml/g \end{aligned}$$

Quality Control:

The optimum working range is 0.1 to 1 ng/ml in solution, equivalent to 10 - 100 ppb in rock.

The determination limit of this method is 5 ppb in rock.

Precision, expressed at the 95% confidence limit (2σ), is ±12% (relative).

The accuracy is comparable to the precision, based on data collected from standard reference material.

Productivity:

A technician should be able to complete 15 to 20 determinations per day.

Additional Notes:

1. Standard solutions and reacting reagents should be kept in glass containers. Avoid using plastic bottles, since most plastic materials contain mercury compound ingredients as plasticizers and will contaminate the solutions.

2. Glassware, such as test tubes, should be cleaned with nitric acid, followed by a rinse with distilled water. (Soaking overnight in 10% nitric acid is quite effective). Glassware known to have been used for samples with high Hg concentrations (>1 ppm) should be cleaned with conc. nitric acid, followed by a rinse with tap water and then distilled water. (Tap water usually contains negligible amounts of Hg. It can safely substitute distilled water for cleaning, although this is not recommended conventionally).

3. Gold, platinum, palladium, arsenic, antimony, bismuth and selenium are known interferents, but are rarely present in concentrations sufficient to cause a significant problems.

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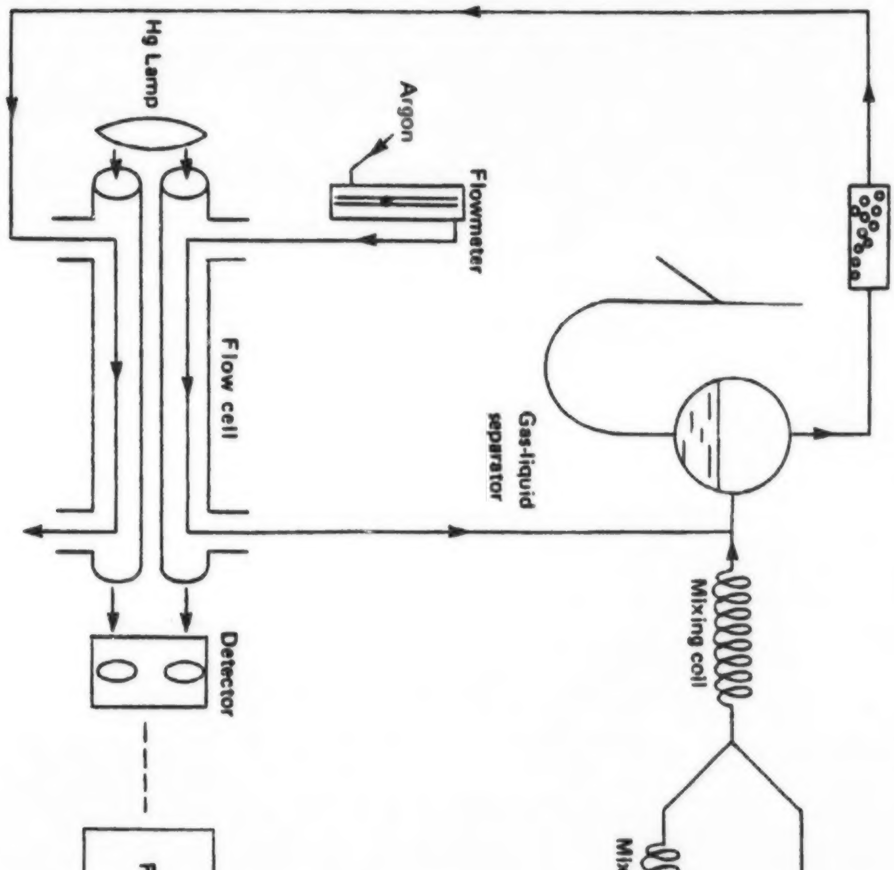

MgClO$_4$ dryer
Argon
Flowmeter
Hg Lamp
Flow cell
Gas-liquid separator
Mixing coil
Detector
Recorder
Mixing coil
(O,O)
(R,R)
(P,W)
(O,O)
(P,W)
Proportioning Pump
SnCl$_2$ 30%
Air
Sample
NH$_2$OH·HCl, 5%
HNO$_3$,10%
Waste
Sampler

Figure Hg1. Automated cold vapour flameless AA system for determination of mercury.

DETERMINATION OF CARBONATE-CARBON (CO_2) COULOMETRIC METHOD

Introduction:

Carbonate-carbon is the main component of total carbon in the majority of geological samples. It is conventional, therefore, to report total carbon as CO_2, as if all the carbon is from carbonate-carbon. In some samples, however, carbonate-carbon can represent only a small part of the total carbon. The remainder of the total carbon is either graphitic, organic carbon, diamond and/or carbide.

In studies of geological processes, it is sometimes necessary to know not only the carbonate-carbon or the total carbon content, but also the non-carbonate carbon in the samples. Total carbon can be determined by inductive furnace-infra-red method (refer to EA12-1). Non-carbonate carbon cannot be determined directly, however, by determining carbonate-carbon, non-carbonate carbon can be calculated by subtracting carbonate-carbon from total carbon.

The determination of carbonate-carbon on the Coulometrics CO_2 Determinator is initiated by heating a known weight (0.05 - 0.50 g depending on the carbonate content) of sample with 2 ml of 2N perchloric acid in the heated reaction tube. The evolved CO_2 is swept by a stream of filtered air into the Coulometrics cell which is filled with a partially aqueous medium containing ethanolamine and a colorimetric indicator.

When CO_2 is passed through the cell solution, it is quantitatively absorbed and converted to a strong (titratable) acid by the ethanolamine causing the colour of the indicator to fade. As soon as this happens, the coulometer electrically generates base to restore the colour.

The accumulated charge (coulombs) is displayed on a digital readout as micrograms of carbon. When the accumulation ceases, the end point is reached. The percent of carbon in a sample is then mathematically converted to percent of CO_2.

Safety advisory:

1. Due to the odor of ethanolamine coming from the coulometer cell, the analytical operation should be performed in a well ventilated area or in a fume hood.

Method:

The method consists of the following techniques:

1. Decomposition of the sample
2. Measurement of CO_2 signal by the Coulometrics CO_2 Determinator
3. Calculation of the results based on weight

Apparatus:

- Coulometrics CO_2 Determinator which consists of:

A. Model 5010 Coulometrics CO_2 Coulometer

B. Model 5030 Carbonate Carbon Apparatus with reaction tubes

Reagents:

- Perchloric acid, $HClO_4$, 2N
- Potassium hydroxide solution, KOH, 45%
- Potassium Iodide solution, KI, 50% KI solution at pH 3
- Coulometer solution
- Anode solution
- Potassium iodide crystals, KI

Procedures:

1. Measurement of carbonate-carbon concentration

1.1. Coulometer set-up

1.1.1. Place approximately 100 ml of coulometer solution in the cell body. (See Figure CC1.).

1.1.2. Add stirring bar.

1.1.3. Place a few crystals of KI inside the anode compartment.

1.1.4. Place the cell cap on the cell body, and add anode solution to the anode compartment so that when the silver electrode is in place, the anode solution level will be the same as the solution level in the cell body.

1.1.5. Place the cell in the coulometer cell holder with the electrodes to the back.

1.1.6. Be sure the cell current switch is off, and turn on coulometer.

1.1.7. The anode compartment frit, and gas inlet tube should be positioned so that they are in the back of the light beam. This may be checked by rotating the cell until maximum %T is observed. The Pt electrode should project out and away from the light beam for highest sensitivity.

1.1.8. Plug in the electrodes noting polarity (cathode - black, anode - red).

1.2. Carbonate-carbon apparatus set-up

Figure CC1 shows the assembled CO_2 apparatus. (For tubing connections, follow the procedure shown in the manufacturer's instruction manual.)

1.2.1. Fill air scrubber with approximately 12 ml of 45% KOH solution.

1.2.2. Fill sample scrubber tube with 50% KI solution.

1.3. Operation

1.3.1. Weigh and transfer sample (0.05 g to 0.50 g depending on the carbonate content) into a sample tube.

1.3.2. Moisten the sample with approximately 0.5 ml of distilled water.

1.3.3. Place the sample tube on the heater of the CO_2 apparatus.

1.3.4. Place the condenser on top of the sample tube.

1.3.5. Be sure system is leak free.

1.3.6. Switch on the air pump and purge the system.

1.3.7. Connect the scrubber outlet of the CO_2 apparatus to the gas inlet of the coulometer cell.

1.3.8. Press the reset button on the coulometer to zero carbon reading.

1.3.9. Press the plunger on the acid dispenser to dispense about 2 ml of acid.

1.3.10. Turn on the heater and adjust heating as desired.

1.3.11. Allow sufficient time (10-30 minutes) for complete reaction, and record carbon reading when coulometer gives a steady maximum reading.

1.3.12. Run a blank by heating 2 ml of 2N $HClO_4$ similarly, but omitting the sample.

2. Calculation of the results

The CO_2 content of the sample is calculated according to the following formula:

$$\% CO_2 = \frac{(Micrograms\ C - blank)}{Micrograms\ sample} \times 366$$

3. Shutdown

3.1. Switch off the air pump of the CO_2 apparatus.

3.2. Disconnect the scrubber outlet line.

3.3. Turn off the heater.

3.4. Turn off the cell current and coulometer power.

3.5. Unplug the electrodes and remove the cell from the holder.

3.6. Dispose the coulometer solution and rinse the cell body.

3.7. Remove the silver electrode and rinse with water.

3.8. Rinse the outside of anode compartment, gas inlet tube and Pt electrode with distilled water.

3.9. Rinse out the anode compartment with acetone. Remove KI and deposits on top of the glass frit.

4. Maintenance

4.1. The cell solutions should be replaced if over 100 mg of carbon have been titrated.

4.2. If the deposits stick in the glass frit, pull acetone through frit with aspirator or other vacuum source, or clean it with ultrasonic cleaner. Anode deposits can be removed with a saturated KI solution.

4.3. If a deposit is evident on the platinum electrode, this should be dissolved in 1:1 HNO_3.

4.4. The cell current switch should be turned off whenever the cell is disconnected.

4.5. A high blank result is usually the result of exhaust KOH solution in air scrubber. Replace the solution when this happens.

Quality control:

The optimum working range for this method is 0.01 - 20%.

The determination limit for CO_2 is 0.01% in rock, although the system is capable of detecting as low as 0.003%.

Precision, expressed at the 95 % confidence limit (2σ), for the mid-range value is ±4% (relative), e.g. 10% ±0.4%.

The accuracy is comparable to the precision based on data collected from standard reference materials.

Productivity:

A technician should be able to complete 20 determinations per day.

Additional Notes:

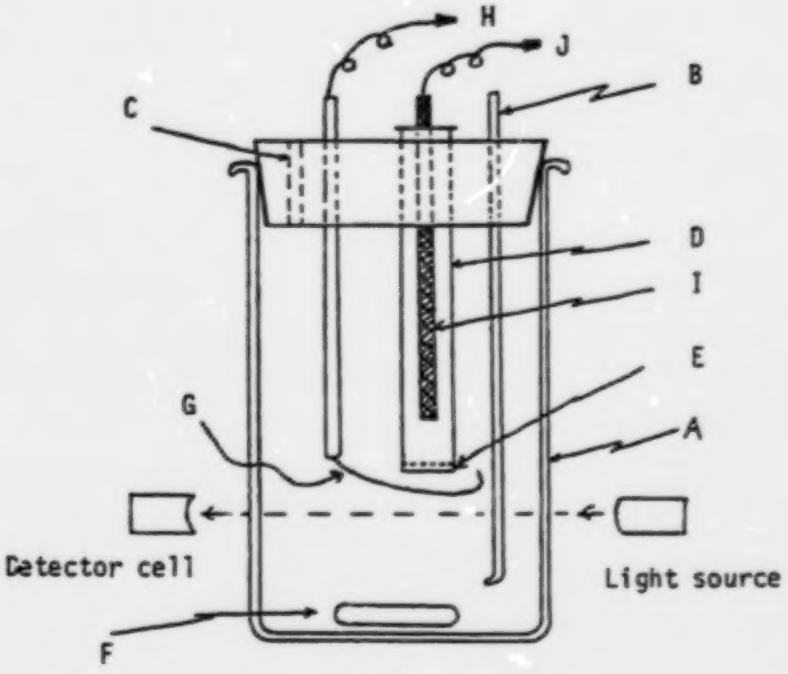
1. Typical blank values are 5-10 µg C/10 min. If a higher value is observed, the air scrubber solution should be changed.
2. Do not wash the anode with water, since the precipitated AgI will plug the frits.
3. Any volatile acid or base not removed by the scrubbing solution will interfere with the analysis. Potentially interfering gases which the scrubber removes include: H_2S, Cl_2, HI, HF, SO_2 and SO_3. Another scrubbing solution which is effective for removai of chlorine and sulphur compounds is a saturated Ag_2SO_4 solution containing 3% H_2O_2 at pH 3.
4. Although running standard samples is not required for calibration, it is desirable to confirm proper operation of the apparatus and coulometer by running standards such as primary standard grade calcium carbonate periodically.
5. Potassium iodide crystals should appear in the anode compartment at all times.
6. A variety of mineral acids can be used for evolution of CO_2. The following acids are most common:
   a. 2N $HClO_4$
   b. 2N H_2SO_4
   c. 2N HCl - care must be taken to insure the HCl gas does not overload the scrubber.

Bibliography:

Instruction Manual for Coulometrics CO_2 Determinator, Coulometrics Incorporated.

Chan, C.Y., 1986, Determination of Carbonate Carbon in 41 International Geochemical Reference Samples by Coulometric Method, Geostandards Newsletter, Vol. X, No. 2, pp 131-134.

Huffman, E.W.D., 1977, Performance of a New Automatic Carbon Dioxide Coulometer, Microchemical Journal, Vol. 22, pp 567-573.


H
J
B
C
D
I
E
G
A
Detector cell
Light source
F

A. Cell body
B. Gas inlet
C. Gas outlet
D. Anode compartment
E. Frit
F. Stirrer
G. Platinum electrode (cathode)
H. Cathode terminal
I. Silver electrode (anode)
J. Anode terminal

Figure CC1. Coulometer cell.

DETERMINATION OF MOISTURE

Introduction:

Minus water (H_2O^-), or moisture, is the portion of water in rocks held by surface forces such as adsorption and capillarity. It can be driven off at 100-110°C. The H_2O^- content is determined by measuring the loss of weight of a 1 g sample when it is dried overnight at 110°C.

Safety advisory:

1. No specific safety advisory is required for this method.

Method:

1. Direct gravimetric determination of loss on heating
2. Calculation based on sample weight loss

Apparatus:

- Drying oven
- Porcelain crucible with lid
- Desiccator

Reagents:

- No reagents are required for this method.

Procedures:

1. Direct gravimetric determination of H_2O^-

1.1. Weigh 1.0000 g of sample and transfer into a pre-dried porcelain crucible.

1.2. Record the total weight of the sample and crucible with cover.

1.3. Heat the sample in an oven at 105° - 110°C for at least one hour (preferably overnight). Partially cover the crucible by tilting the lid to the side.

1.4. Fully cover, then remove the crucible and quickly place it in a desiccator. Let cool to room temperature.

1.5. Weigh the dried sample and the crucible with the lid as quickly as possible to avoid moisture being re-absorbed by the sample.

2. Calculation of the results

The difference in weight, before and after drying, represents the amount of moisture, or minus water, in the sample.

$$\textit{Percent of minus water} = \frac{w_1 - w_2}{w} \times 100$$

where, w = original wt. of the sample

w_1 = wt. of original sample + crucible with lid

w_2 = wt. of dried sample + crucible with lid

Quality Control:

The determination limit for this method is 0.01%.

Accuracy and precision have not been established.

Productivity:

A technician should be able to complete 40 determinations per day.

Bibliography:

Maxwell, J.A., Rock and Mineral Analysis, Interscience Publishers, 1968, 584 pages.

Potts, P.J., A Handbook of Silicate Rock Analysis, Blackie and Sons Limited, Glasgow, 1987, 622 pages.

DETERMINATION OF ACID INSOLUBLE RESIDUE

Introduction:

This method is used as a relative measure of impurities in carbonate samples. In most samples silica will predominate in the acid insoluble residue. The amount of residue obtained depends upon the acid used, the time and temperature of the digestion and the grain-size of the sample. The conditions under which the determinations are made should be consistent and well defined.

Safety advisory:

1. The following operations should be performed in a fume hood:

   A. Preparation of HCl solution

   B. Addition of the (1:3) HCl solution to the samples

   C. Heating and digesting on a hot plate

2. The MSDS sheet pertaining to the use of hydrochloric acid must be reviewed before proceeding. Safety procedures as outlined in the Geoscience Laboratories' Safety Manual should also be reviewed.

Method:

The method consists of the following techniques:

1. Sample decomposition and ignition of residue.
2. Direct gravimetric determination of the residue remaining after the weighed sample is digested with hydrochloric acid and the residue ignited.
3. Calculation based on the sample weight loss.

Apparatus:

- Glass beakers, 150 ml
- Hot plate
- Porcelain crucibles, 30 ml, with lids
- Glass filtering funnels
- Funnel supports
- Filter papers, Whatman No. 40, 11 cm

Reagents:

- Hydrochloric acid, HCl, (1:3)
- Hydrochloric acid, HCl, (5:95)

Procedures:

1. Reagent preparation

1.1. (1:3) HCl solution - Prepare 1 liter of this solution by mixing 250 ml of concentrated HCl with 750 ml of distilled water.

1.2. (5:95) HCl solution - Prepare 1 liter of this solution by mixing 50 ml of concentrated HCl with 950 ml of distilled water.

2. Sample decomposition and ignition of residue

2.1. Weigh exactly 0.500 g of sample and transfer to a 150 ml beaker.

2.2. Slowly add 50 ml (1:3) HCl. Swirl occasionally.

2.3. When vigorous effervescence has ceased, heat the contents on a hot plate to near boiling. Digest for 15 minutes at a temperature just below boiling.

2.4. Filter at once through a 11 cm Whatman No. 40 filter paper and wash the paper and residue thoroughly with hot dilute HCl (5:95).

2.5. Transfer the paper and residue to a weighed porcelain crucible.

2.6. Burn off the paper at 250° to 300°C, and then ignite the residue at 900° - 1000°C for 15 minutes.

2.7. Cool in a desiccator for half an hour and weigh.

3. Calculation of the results

The content of acid insoluble residue, or acid insolubles, is calculated according to the equation:

$$\text{Acid Insolubles} = 2(w_2 - w_1) \times 100\%$$

where, w_1 = weight of crucible in g,

w_2 = weight of crucible and residue in g after ignition

Quality control:

The determination limit for this method is 0.2%.

The precision, at the 95% confidence limit (2σ) is ±5% (relative).

Accuracy has not been determined since a suitable standard reference material is not available.

Productivity:

A technician should be able to complete 20 determinations per day.

Additional Notes:

1. Samples are analyzed simultaneously in a batch of 12 or more, depending on the availability of working space.

2. The method does not determine organic insoluble residues as these would be destroyed in the combustion stage.

Bibliography:

Maxwell, J.A., Rock and Mineral Analysis, Wiley Interscience Publishers, 1968, pp 304-305 and pp 487-488.

Potts, P.J., A Handbook of Silicate Rock Analysis, Blackie and Sons Limited, Glasglow, 1987, 622 pages.

DETERMINATION OF THE CALCITE TO DOLOMITE RATIO CHITTICK APPARATUS METHOD

Introduction:

The determination of the carbonate content and calcite/dolomite ratio of sedimentary rocks and tills, provides valuable information enabling the geologist to classify the materials and determine their suitability as materials for use in the construction industry. The concentrations of these minerals are highly variable in rocks and tills.

The method is based on the different reaction rates of calcite and dolomite in hydrochloric acid. The ratio of calcite to dolomite in a finely ground sample (minus 200 mesh) can be determined by taking two readings of the volume of evolved CO_2 in a Chittick gasometric apparatus. The first reading records gas evolved principally from the faster reacting calcite, the second reading records the gas evolved from both minerals.

Safety advisory:

1. This method involves the specific use of hydrochloric acid. Staff must read the MSDS sheet on hydrochloric acid, and review all safety procedures required for this chemical. The (1:1) HCl should be prepared in a fume hood to avoid inhaling acid fumes.

Method:

The method consists of the following techniques:

1. Sample decomposition by HCl attack
2. Measurement of CO_2 gas evolved
3. Calculation of the results based on an accepted formula

Apparatus:

- Chittick gasometric apparatus (Fig. Ch1) which consists of the following components:
  - A. Decomposition flask, 250 ml
  - B. Graduated 20 ml pipette with stopcock at the base
  - C. Stopcock
  - D. Gas measuring tube
  - E. Levelling bulb
  - F. Magnetic stirrer and stirring bar (4 cm in length)

Reagents:

- Hydrochloric acid, HCl, (1:1)
- Methyl orange indicator
- Displacement solution

Procedures:

1. Reagent preparation

1.1. (1:1) HCl solution - Mix 500 ml of concentrated HCl with 500 ml of distilled water.

1.2. Methyl orange indicator - Dissolve 0.05 g methyl orange in distilled water and dilute to 100 ml with distilled water.

1.3.1. Displacement solution - Dissolve 100 g NaCl in 350 ml distilled water.

1.3.2. Add 1 g $NaHCO_3$ and 2 ml methyl orange indicator, and then sufficient HCl to make just acid (decided pink). Stir until all CO_2 is removed.

1.3.3. This solution is used in the gas measuring tube and levelling bulb and seldom needs to be replaced.

2. Sample decomposition

2.1. Weigh 1.700 g of the -200 mesh sample (0.850 g in case the sample contains more than 40 percent carbonates), and place it in the decomposition flask (A in Figure CH1).

2.2. Connect the flask to the Chittick apparatus. Open the stopcock (C) and bring the displacement solution in the measuring tube (D) to the 20 ml mark above the zero, by raising or lowering the levelling bulb (E).

2.3. The pipette (B) is filled to the zero mark with (1:1) HCl.

2.4. Close the stopcock (C) and lower the levelling bulb somewhat to reduce the pressure within the apparatus.

2.5. Open the stopcock of the pipette and let 20 ml of the (1:1) HCl run into the decomposition flask as quickly as possible.

2.6. Switch on the magnetic stirrer to secure intimate mixture of the contents. At the same time lower the levelling bulb.

2.7. During decomposition, prevent the liberated CO_2 from escaping through the pipette by keeping the displacement solution in the levelling bulb at a lower level (about an inch lower) than that in the gas measuring tube at all times.

2.8. After having dispensed 20 ml of (1:1) HCl into the decomposition flask, close the stopcock of the pipette.

3. Measurement of Evolved CO_2 Gas

3.1. Exactly 30 seconds after the delivery started, equalize the levels of the displacement solution in the levelling bulb and the measuring tube, and take the first reading of the volume of CO_2.

3.2. Then lower the levelling bulb again until the evolution of CO_2 has ceased completely (20 minutes is usually required for complete decomposition).

3.3. After 30 minutes take the second reading of the volume of CO_2.

3.4. Observe the temperature of the air surrounding the apparatus and also the barometric pressure at the time of the reading.

3.5. Find the correction factor for temperature and pressure from the table (see 'Association of Official Agricultural Chemists', 1955, pp 945-951.).

4. Recording and Calculation of the results

A record (Form CH1) is kept of the following readings, correction factors, and the computed results for each sample.

A. Sample Number

B. Weight of sample analyzed (usually 0.850 g or 1.700 g)

C. Room temperature

D. Correction factor for the temperature

E. First reading:

  (a) volume of CO_2
  (b) corrected first reading (obtained by multiplying the first reading by its correction factor)

F. Second reading:

  (a) volume of CO_2
  (b) corrected second reading (obtained by multiplying the second reading by its correction factor)

G. Calulation: Corrected second reading minus corrected first reading, or Fb - Eb.

H. Corrected first reading minus 4 percent of the value of (G).

I. 4 percent of the value of (G) is added to (G).

One tenth of the values of (H) and (I) represent the percent CO_2 from calcite and dolomite respectively when the 1.700 g sample weight is used (see Association of Official Agricultural Chemists, 1955, pp 127-128). The values are doubled if 0.850 g of sample is used. Convert percent of CO_2 (from calcite) to calcite by multiplying by a factor of 2.275, and percent CO_2 (from dolomite) to dolomite by multiplying by a factor of 2.095. The sum of the carbonates and the ratio of calcite to dolomite are also calculated.

Quality Control:

The optimum working range for this method is 5% to 40% total carbonate.

The determination limit for both calcite and dolomite is approximately 0.5%.

The precision at mid-range is 1.5% at the 95% confidence level (2σ), e.g. 20% ± 1.5%.

Productivity:

A technician should be able to complete 25 determinations per day working on two sets of Chittick apparatus simultaneously.

Additional Notes:

1. The method is simple, but lacks accuracy and has poor precision. There are many sources of error which cannot be eliminated such as the presence of water vapor in the Chittick apparatus, the presence of carbonates other than calcite or

dolomite in the sample, and the inconsistency of speed of reaction.

Although the determination limit is expected to be about 0.2% calcite or dolomite (equivalent to 1 ml of evolved CO_2) the Laboratories has found that for samples with less than 4% total carbonate the reproducibility of results is poor.

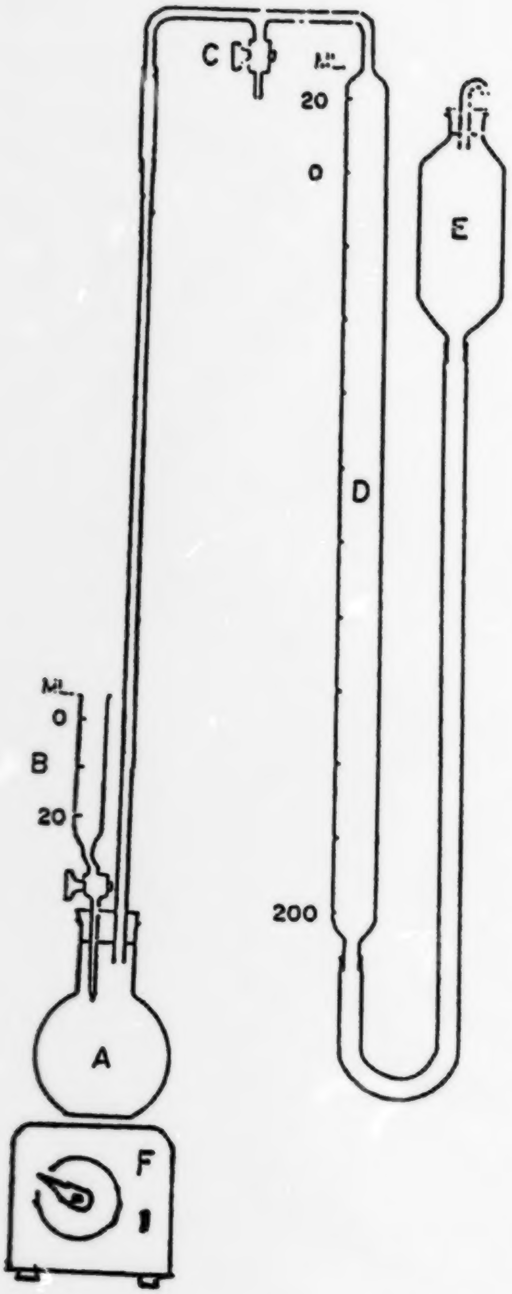
When one mineral (calcite or dolomite) predominates, the ratio is liable to considerable error even though the determination of the major component may be quite precise. If the concentration of either mineral is below the determination limit the ratio can only be expressed as > or < the value obtained using the limit.

2. In calculating the percent of CO_2 from dolomite, 4 percent of the difference between the corrected first and second readings is added in order to compensate the CO_2 that is derived from dolomite, yet liberated in the initial 30 seconds.
3. In analyzing a large number of samples, two Chittick apparati may be operated simultaneously. This would increase production substantially.
4. Barometric pressure change is normally very small, hence a pressure correction step may be omitted.
5. Care must be taken to rinse the decomposition flask thoroughly with water after each analysis, since the slightest trace of acid left in the flask will cause some decomposition before the operator has a chance to connect the flask with the rest of the apparatus. Moreover, the upper part of the flask should be dried after washing to prevent any of the powdered sample adhering to the sides or the neck of the flask.

Bibliography:

Official Methods of Analysis of the Association of Official Agricultural Chemists, 8th Edition, 1955, pp 127-128 and page 947-951.

Dreimanis, A., 1962, Quantitative Gasometric Determination of Calcite and Dolomite by Using Chittick Apparatus; Journal of Sedimentary Petrology, Vol. 32, No. 3, pp 520-529.


C
ML
20
0
E
D
200
ML
0
B
20
A
F

A - **Decomposition Flask**
B - **Pipet**
C - **Stopcock**
D - **Gas-measuring Tube**
E - **Levelling Bulb**
F - **Magnetic Stirrer and Magnet**

Figure CH1. Chittick Gasometric Apparatus

Ontario

Ministry of
Natural
Resources

Mineral
Research
Branch

Carbonate Analysis
by
Chittick Method

Job No.

Barometric Pressure

Submitted by

Date

Sample No.	Weight (gm.)	1st Reading			2nd Reading			% CO_2	% CO_2	2.275 (factor)	2.095 (factor)	Total	Ratio
		ml.	Corr. Factor	Corr. ml.	ml.	Corr. Factor	Corr. ml.	from Calcite	from Dolomite	% Calcite	% Dolomite	Carbonate	Calcite / Dolomite

Form MS 913 (08/79)

Form CH1.